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IN ENGLISH TRANSLATION



CONSULTANTS BUREAU

Corrosion of Chemical Apparatus

CONTAINING information heretofore unavailable in one volume in English, this recent monograph is a result of the investigations carried out by the authors at the Scientific Research Institute of Chemical Machines and the Moscow Institute of Chemical Machines.

Here they present valuable data concerning the theory of intercrystalline and stress corrosion, and then discuss in detail the causes and character of corrosion cracking of carbon steels, alloyed steels, and nonferrous metals. This information is based not only on Schwartz and Kristal's extensive studies of various cases of destruction of apparatus and machinery of the chemical and allied branches of Soviet industry, but also on recent literature in the field, including 219 references of which most are to the Soviet literature.

By noting certain regularities of behavior of metals while conducting their investigations, the authors were able to include in their book many practical recommendations on methods of prevention and protection against cracking and intercrystalline corrosion of metals, thus providing a more efficient approach to the problem of choice of materials for the manufacture and assembly of chemical apparatus.

1959

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256 pages

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CHAPTER I. CAUSES OF

CORROSION CRACKING OF METALS

Effect of factors relative to the structure and properties of metals and alloys and diffusion processes taking place in metals and alloys; effect of industrial treatments on metals during manufacturing of finished products; effect of the surface state; effect of the nature, concentration and temperature of the aggressive medium; effect of the nature, amount and distribution of stresses; mechanism of corrosion cracking of metals and alloys; conclusions.

CHAPTER II. CORROSION

CRACKING OF CARBON AND ALLOYED STEELS

(up to 10% of alloyed elements)

Effect of the composition and structure of the steel; effect of the nature of the aggressive medium; conclusions.

CHAPTER III. CORROSION

CRACKING OF STAINLESS STEELS

Chromium Steels: Intercrystalline corrosion of chromium steels; corrosion of chromium steels under static stress.

Chromium Nickel Steels: Intercrystalline corrosion of austenitic and austenitic-ferritic chromium-nickel steels; Intercrystalline corrosion of the metal in the welded seam and in the heat-affected zone; corrosion of chromium nickel austenitic steels under static stress; conclusions.

CHAPTER IV. CORROSION OF NON-FERROUS METALS AND ALLOYS

Aluminum and aluminum alloys; copper and copper alloys; nickel and nickel alloys; magnesium, and magnesium alloys; lead; titanium; cracking of other metals; conclusion.

CHAPTER V. METHODS OF PROTECTION AGAINST CORROSION CRACKING

Protection of stressed metals against corrosion cracking; methods of protection of metals against intercrystalline corrosion; conclusions.

CHAPTER VI. TESTING METHODS

Methods of testing resistance to corrosion under stress; methods of testing susceptibility to intercrystalline corrosion; conclusions.

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NIKOLAI SEMENOVICH KURNAKOV (CENTENNIAL)

Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
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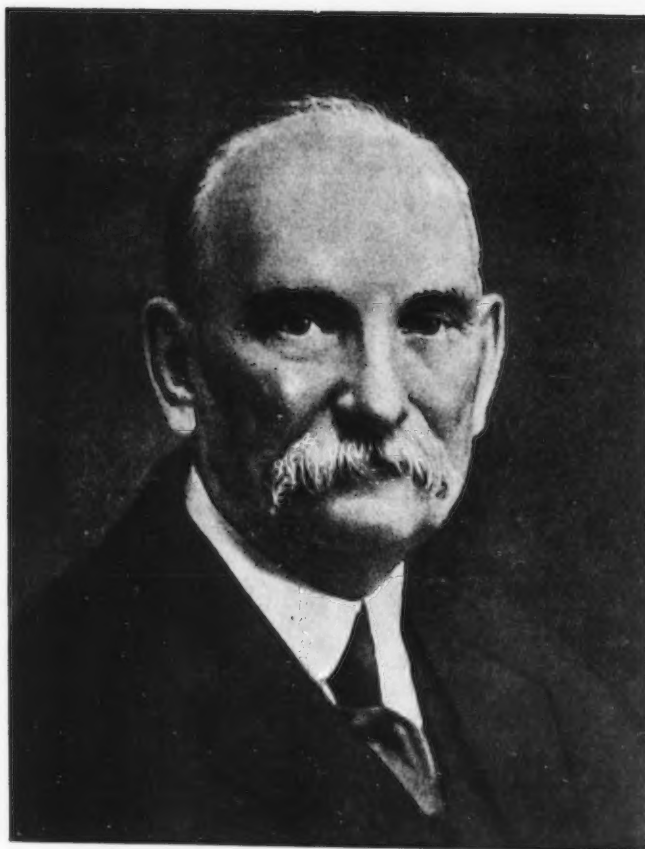
Nikolai Semenovitch Kurnakov, who became one of the outstanding physical chemists of our times, was born on November 24, 1860 in Nolinsk (in Vyatsk county). Kurnakov's interest in science appeared very early. At the age of 14 he installed a chemical laboratory in his home and carried out a series of experiments in preparative and analytical chemistry, using as a guide "School Chemistry" by Stendart and "Chemical Laboratory" by Stammer. On leaving the Nizhnegorodsk Military Gymnasium in 1877, Kurankov entered the metallurgical department of the St. Petersburg Mining Institute and graduated in 1882 as a mining engineer. His interest in chemistry, which had appeared in his childhood years, increased during his student days at the Mining Institute and in 1880 his two first papers "The Crystal Forms of Alums" and "The Crystal Forms of Schlippe's Salt" ($\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$), were published in the Records of the Mineralogical Society.

The talented student was immediately noticed by the Mining Institute's faculty (D. K. Sushin, K. I. Lisenko, and Acad. N. I. Kashkarov) and after completing his studies, Kurnakov remained in the Institute's chemical laboratory. The same year N. S. Kurnakov, together with Prof. N. A. Iossa, was sent to the Altai copper works and the main results of this trip were published in 1884 in the Mining Journal as a voluminous article "Smelting of Copper, Lead, and Silver in the Altai Plants." In 1883 N. S. Kurnakov was sent by the Mining Institute to Germany to study the salt industry, metallurgy, and analysis. The time Kurnakov spent abroad was a very well used: he worked in laboratories, attended lectures in the Freiberg Mining Academy (Profs. Winkler, Ledebuhr, and Richter), and studied the operation of salt works in Prussia, Lorraine, Wurtemberg, Baden, Bavaria, and Tyrol. The extensive material gathered during his stay abroad was the basis for the major work "Salt-Pan Evaporation Systems," which was presented to the Board of the Mining Institute as a dissertation for an assistantship in the department of metallurgy, halurgy, and analysis.

Besides his work with students on technical analysis and assaying and lectures on halurgy, fuel technology, and general metallurgy, Kurnakov's activities as Assistant in the Mining Institute from 1885 to 1893 included the beginnings of his independent scientific activity and a series of scientific studies of platinum, cobalt, and molybdenum salts, thiourea compounds, the composition of air and firedamp from coal pits of the Donets Basin, etc., as well as the publication of a course of lectures on the salt industry.

In 1893 Kurnakov wrote a dissertation on "Complex Metal Bases" for a professorship in the Mining Institute. In this extensive work he examined thoroughly the nature of complex metal bases and critically analyzed existing theories on their structure. In experimental investigations of the complex compounds of platinum metals with thiourea and thioacetamide, a number of properties are generally used, namely, the crystal structure, solubility, refractive indices, the behavior of the compound synthesized toward various reagents, etc. By using a great variety of investigation methods, Kurnakov subsequently was able to make broad generalizations on the determination of the relation between the properties of chemical diagrams and the phases formed during chemical reactions and to establish a new, independent field, namely that of physicochemical analysis. In 1903 he developed his own design of a photorecording pyrometer for thermal investigations.

The range of his work and possibility of carrying it out increased appreciably when Kurnakov was appointed professor in the Mining Institute, then professor of physical chemistry in the Electrotechnical Institute (1899-1908), and particularly when he was elected professor of general chemistry in the Petersburg Polytechnic Institute (1902-1930). During the organization of the Petersburg Polytechnic Institute, Kurnakov, together with Mendeleev, Menshutkin, and Walden, participated very actively in the establishment of chemical laboratories and in the teaching of chemistry. About this time he published a whole series of papers on the investigation of salt brine from the Kuyal'nitsk and Khadzhibeisk estuaries and Genichesk and Perekop salt lakes; on the conditions for converting Glauber's salt into thenardite in salt lakes and, finally, on the conditions for extracting Glauber's salt in Kara-Bogaz. The work in Kara-Bogaz was a shining example of the scientific solution of the problem of the periodic formation of Glauber's salt. The immense value of Kara-Bogaz as the greatest deposit of Glauber's salt in the world and a limitless source for the industrial extraction of sulfate was established in subsequent expeditions in 1909 (with the



NIKOLAI SEMENOVICH KURNAKOV

participation of N. I. Podkopaev). More detailed information on Kara-Bogaz was published in 1916 in a collection on Kara-Bogaz in the Proceedings of the commission on the natural resources of Russia and substantiated by the study, carried out in 1917 with the help of S. F. Zhemchuzhnyi, of the system magnesium sulfate-sodium chloride-water, which is a typical subject for physicochemical analysis. The investigations started by Kurnakov and the data obtained on Kara-Bogaz are still valuable and remain a classical example of the close relationship of science and industry.

We should note that to a considerable extent, the establishment of new and the extension of existing chemical laboratories in the Mining, Polytechnic, and Electrochemical Institutes were due to the indefatigable activity of Kurnakov who considered that well-equipped chemical laboratories were most important for scientific research. In this connection he was particularly successful in the Petersburg Polytechnic Institute where the chemical laboratories of the general chemistry department were for a long time unsurpassed both in area and equipment.

At that time his intense activity and unusual enthusiasm in solving complex scientific problems attracted to Nikolai Semenovich Kurnakov numerous co-workers. His students S. F. Zhemchuzhnyi, N. A. Pushin, N. I. Podkopaev, G. Yu. Zhukovskii, N. S. Kostantinov, G. G. Urazov, N. I. Stepanov, A. N. Kuznetsov, N. N. Efremov, N. N. Beketov, K. F. Beloglazov, etc., have contributed a great deal to the study of metal alloys, salt deposits, complex compounds, chemistry of platinum metals, and to the establishment of the principles and theory of physicochemical analysis. The diversity of Kurnakov's activities and scope of the problems and thoroughness with which he treated them are astounding, the more so as in 1909 he was appointed a member of the Scientific Mining Committee, a member of the Permanent Committee on the Investigation of Firedamp, chairman of the Committee on the Investigation of the Explosive Properties of Coal Dust in the Donets mines, a permanent member of the Board of Editors of *Zeitschrift für Anorganische Chemie*, a member of the council of the *Société Chimique*, a member of the International Commission on the Nomenclature of Inorganic Compounds, etc. With all this diversity of work, Kurnakov still eagerly accepted problems of a purely practical nature. Thus, his work with G. G. Urazov on cases of poisoning of persons during the transportation of ferrosilicon developed into a strictly scientific determination of the causes, which were found to be the presence of definite, toxic impurities in commercial grades of ferrosilicon.

The rare ability and breadth of knowledge and views of Kurnakov attracted the attention of D. I. Mendeleev who several times proposed that Kurnakov join him as a helper in scientific work. However, by the Kurnakov's interest were already defined and had taken a new, independent direction so that he felt unable to change either this direction or the tenor of his activities.

On December 7, 1913 the Russian Academy of Sciences elected N. S. Kurnakov as ordinary academician of chemistry and in 1922 he became a member of the Gottingen Academy in Germany. His election as academician allowed him to increase his participation in the organization of the commission on the study of the natural resources of Russia (KEPS), in the general chemistry laboratory of the Academy of Sciences, and in the creation of the Institute of Physicochemical Analysis and the Institute for the Study of Platinum and Other Noble Metals. With the transfer of the Academy of Sciences from Leningrad to Moscow in 1934, these institutes were combined into the Institute of General and Inorganic Chemistry which is named after N. S. Kurnakov.

Kurnakov's broad knowledge in various fields was demonstrated particularly well in his lectures and organization of research in departments which attracted many students for diploma work in chemistry. His authority as an outstanding scientist and teacher was extremely high. The number of students applying for diploma work in his laboratory was so numerous that a special list was drawn up of the candidates waiting for places. Kurnakov considered it absolutely necessary for all scientific workers to combine research with study in institutes of higher education and all his students, whom he selected with particular care, simultaneously carried out extensive research work and attended a course on some subject in a university or college.

Very characteristic of his activities was the publication of periodic collections: *Izvestiya of the Institute of Physicochemical Analysis* and *Izvestiya of the Institute of Platinum and Other Noble Metals*. The contents of these collections are exceptionally interesting as they reflect in historical sequence the continuous growth and the state of knowledge in these fields and the advances achieved during the establishment and growth of the two new institutes. In addition to the main investigations, these collections contained translated articles on methods of representing chemical diagrams, abstracts of the most interesting papers and reviews, brief reports of scientific meetings, etc. The interesting content and thoroughness of the preparation of the collections was mainly the result of the work of the editors B. N. Menshutkin and E. Kh. Fritsman, who were excellent helpers of Kurnakov.

Regrettably, the publication of these valuable scientific collections ceased in 1955-1956 and thus the possibility of a more detailed account of the work in order to popularize it has decreased considerably. The contents of both collections were widely commented upon in the foreign literature and clearly illustrated the growth and development of the concept of physicochemical analysis and the theory of complex compounds of platinum metals.

Kurnakov attached much value to the development of the idea of physicochemical analysis and in carrying out research, he considered not only the importance of the subject being studied or the phases obtained, but also paid particular attention to the type of diagram obtained, the conditions characterizing the formation of chemical compounds, and confirmations of a relation between the geometric elements of a chemical diagram and the definite phases formed during chemical reactions of the system. The aim of the so-called "general section" of the Institute of Physicochemical Analysis, which was then directed personally by Kurnakov and N. I. Stepanov, was the development of the theory of physicochemical analysis and the procedures and the study of the properties of chemical diagrams. Naturally, the greatest role in these problems was played by the initiator of physicochemical analysis, N. S. Kurnakov, who published a number of papers, namely, "Topology of a Chemical Equilibrium Diagram," "Compounds and Space," "Introduction to Physicochemical Analysis," "Singular Elements of Chemical Diagrams," etc. One of Kurnakov's closest students, Corresponding Member N. I. Stepanov, carried out a series of investigations on the metrics of chemical diagrams. This section also includes a series of investigations on methods of representing systems with many variables (V. Ya. Anosov) and on polythermal polyhedra of complex systems (C. Z. Makarov), the general theoretical conclusions drawn from investigations of complex, multicomponent systems and of simple and reciprocal systems without solvent (A. G. Bergman) systematic investigations of electrical conductivity for use in physicochemical analysis (M. A. Klochko), etc.

Kurnakov's fundamental principles on the triangulation of chemical diagrams made it possible to interpret the complex polythermal chemical diagrams obtained during investigations.

In this work it was stressed that "the term physicochemical analysis, introduced into science by Kurnakov. . . covers a new, extensive section of general chemistry whose aim is the study of the relation between a measurable property of equilibrium systems formed by two or more independent substances or components and the composition of the mixture. The most characteristic feature of physicochemical analysis should be regarded as the application of geometry to the study of the relations between composition and the properties of equilibrium systems. The new methods of physicochemical analysis make it possible to solve problems of physicochemical relations and the chemical nature of solid, liquid, and gas phases, without having to resort to the operations previously used for their separation and purification" (N. I. Stepanov). The great advantage of procedures for investigating phases without their isolation, which is required in all preparative work, was rapidly recognized by numerous investigators and put to exceptionally wide use in various fields of chemistry. One may state without exaggeration that hardly any investigation in the field of theoretical and applied chemistry can do without the use of a "composition-property diagram."

Another subject that interested Kurnakov for a long time was the study of metal equilibria, which was concentrated in the metal equilibrium section, he organized under the direction of G. G. Urazov. These investigations, which were started by Kurnakov and his students S. F. Zhemchuzhnyi, N. A. Pushin, N. S. Konstantinov, N. I. Stepanov, P. Ya. Sal'dau, N. V. Ageev, A. T. Grigor'ev, S. A. Pogodin, V. A. Nemilov, etc., have revealed the extensive variety of diagrams of binary and ternary systems, and the variety and complexity of solid-state conversions of metal alloys, which are of practical use. The wise use of a number of physicochemical properties such as flow pressure, hardness of tempered and annealed alloys, microstructure, electrical conductivity and resistance, x-ray structure, etc., have clearly characterized the solid phases formed, namely, solid solutions with continuous and limited solubility, definite chemical compounds and, finally, compounds of the so-called "berthollide type." At the present time berthollides are regarded as chemical compounds of variable composition occupying a position between compounds with a constant composition and solid solutions. In the same way these phases may be considered as solid solutions which are based on compounds of constant composition that are in a state of dissociation or, finally, as solid solutions of unstable chemical compounds of constant composition. This type of phase was studied with many systems (G. G. Urazov, S. F. Zhemchuzhnyi, N. I. Stepanov, S. A. Pogodin, P. Ya. Sal'dau, V. A. Nemilov, A. T. Grigor'ev, etc.). By using x-ray structural analysis, crystallochemical investigations, and the electronic theory of metals, it was possible to determine the nature and rules of formation of berthollides and their structure and properties (S. T. Kono Konobeevskii, G. V. Kurdyumov, N. V. Ageev, Ya. S. Umanskii, etc.). The third activity of Kurnakov was an extremely fruitful systematic study of salt equilibria, salt lakes, and salt deposits. In addition to numerous works on Kara-Bogaz (S. F. Zhemchuzhnyi, N. I. Podkopaev), N. S. Kurnakov directed a large number of investigations of

singular elements of chemical diagrams (V. I. Nikolaev, M. I. Ravich, L. G. Berg, B. A. Moromtsev, etc.) and isothermal and polythermal diagrams in the department of salt equilibria (V. I. Nikolaev and then S. Z. Makarov) which he established. The most interesting work was that carried out with V. I. Nikolaev on metastable equilibria with the creation of the so-called "solar type of diagram" and that on the sulfate-sodium carbonate equilibria of salt lakes of the Kulunda Steppe (S. Z. Makarov), El'ton lake and the lakes of the Volga delta (B. L. Ronkin, V. I. Nikolaev, V. G. Kuznetsov), Batalpashinsk lakes (M. A. Klochko), lakes of the Ural-Emba region (A. V. Nikolaev, V. I. Nikolaev, I. N. Lepeshkov, etc.). An extensive group of examples of solid solutions was discovered by Kurnakov et al., when investigating salt equilibria. The most interesting of these were the so-called microdisperse solid solutions formed by nickel, cobalt, and manganese salts (V. S. Egorov, N. K. Voskresenskaya, and N. P. Luzhnaya). The study of the cycles of many lakes made it possible for the first time to construct multidimensional physicochemical diagrams by the method of four dimensional systems of coordinates, which later became quite usual.

Kurnakov was very responsive to all questions of a practical nature and was a pioneer in the fundamental problems of the national economy. Thus, as early as 1916-1917 Kurnakov and K. F. Beloglazov analyzed samples of brine and salts in the Mining Institute and on the basis of the data obtained, published the paper "Location of the Potassium Mineral, Potassium Chloride, or Sylvine in Russian" and the paper "Potassium Chloride Deposit of the Solikamsk Salt-Bearing Strata" about the deposit discovered by the geologist P. I. Preobrazhenskii in the Solikamsk Region. In 1922 Kurnakov again returned to this problem in the paper "Potassium Salts and Brines of the Solikamsk Region." These papers were very important in confirming the presence of potassium in the Solikamsk area. The processing of a complicated salt complex requires much work and the study of multicomponent systems in a wide range of temperatures. The classical work of D'Ans and van't Hoff was not sufficient and Kurnakov directed a number of his co-workers to study five-component reciprocal aqueous systems in the temperature range from 0 to 100°. In this connection the work started by O. K. Yanat'eva, at the instigation of Kurnakov, on the so-called "marine system" deserves to be mentioned.

Kurnakov paid much attention to the complex compound section in which the complex compounds of platinum metals were studied initially. The investigation of complex compounds of platinum metals was begun by L. A. Chugaev and continued by his students I. I. Chernyaev, A. A. Grinberg, V. V. Lebedinskii, N. K. Pshenitsyn, etc. The course for the study of complex compounds set by Kurnakov was followed strictly and as a result of the work carried out by a large number of persons headed by I. I. Chernyaev and A. A. Grinberg, numerous examples of complex compounds of platinum metals were prepared and these brought renown to Russian science in this field and made it possible to organize in the Soviet Union the processing of platinum ores and platinum concentrates and the refining and preparation of spectrally pure metals.

The diverse and fruitful activity of Kurnakov was acknowledged in 1940 when he was given the title of Esteemed Scientist of the RSFSR and in 1941 he was awarded the Stalin Prize.

The importance of the investigation method and the basic principles of physicochemical analysis for the solution of practical problems and development of technological schemes was so evident that during Kurnakov's appointment as director of the State Institute of Applied Chemistry and consultant to the All-Union Aluminum-Magnesium Institute, All-Union Institute of Halurgy, etc., the research carried out in these institutes was largely concerned with physicochemical analysis. In these and other institutes Kurnakov and his co-workers gave lectures, directed seminar work, and trained new personnel in physicochemical analysis.

A practical demonstration of the advantages of applying physicochemical analysis was very clearly shown in the numerous reports given by Kurnakov and his students at Mendeleev Congresses, conferences on metallurgy (1920-1924), salts (1928), and metal solid solutions (1929), a conference specifically on physicochemical analysis (1938), and others which he organized. Scientists from all over the country and sometimes from abroad met at these conferences and congresses. It was a pleasure to see that the seeds sown by Kurnakov—the ideas and methods of physicochemical analysis—brought forth tangible results in the form of excellent work, carried out by physicochemical analysts according to Kurnakov's principles. The immense effect of Kurnakov's ideas on the development of physicochemical analysis abroad and his contributions on the characteristics of definite chemical compounds, phases of variable composition, singular elements of chemical diagrams, and water of crystallization have been noted many times by the well-known investigator G. Tamman. There are no significant textbooks on inorganic chemistry and physicochemical analysis abroad which do not mention Kurnakov many times for work whose value and quality still remains.

At present, during the vigorous development of science in the Soviet Union, the ideas of Kurnakov on physicochemical analysis are generally recognized and widely used and are being applied successfully within the system of the Academy of Sciences of the USSR in new fields of chemistry for the solution of problems in the chemistry of peroxide compounds (S. Z. Makarov) and the chemistry of hydrides (V. I. Mikheev).

An immense talent, a variety of scientific interests, a broad outlook, the ability to make wide generalizations and introduce ideas from other fields into physicochemical analysis, attention to the problems and needs of the national economy, a strictly scientific approach to complex problems all characterize Nikolai Semenovich Kurnakov. His inexhaustable and fruitful activity may serve as an example both for his closest students and for all working in the field of physicochemical analysis on problems of general and inorganic chemistry.

ANATOLII FEDOROVICH KAPUSTINSKII (OBITUARY)

Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No. 12, pp. 2080-2081, December, 1960



ANATOLII FEDOROVICH KAPUSTINSKII

Soviet chemical science has suffered a great loss. Corresponding Member of the Acad. Sci. USSR Anatolii Fedorovich Kapustinskii, an outstanding Soviet chemist has died prematurely at the age of 54. His name is connected with a series of broad generalizations in the field of inorganic and physical chemistry. His lucid and very original investigations gave results which were outstanding in simplicity and cogency. Kapustinskii's work combined the methods of structural chemistry and thermodynamics. This combination was a particular feature of his extensive contributions to chemical science.

A. F. Kapustinskii was born on December 29, 1906 in Zhitomir. In 1914 he entered the Warsaw primary gymnasium and in 1922 finished a secondary school in Moscow. In 1923 he became a student in the chemical section of the Physics and Mathematics Department of Moscow State University. In 1929 he graduated from the chemical department of the university. Kapustinskii was the student of the esteemed Academician I. A. Kablukov and Academician E. V. Britske. After completing his university studies, Kapustinskii worked from 1929 to 1941 in the Institute of Applied Mineralogy (now the All-Union Institute of Raw Material) in Moscow, first as laboratory assistant in E. V. Britske's laboratory and then as a candidate, as an engineer, as senior scientist, director of the laboratory and then of the section, and as scientific consultant. In 1935 he was sent to western Europe and the USA. He worked for half a year in the laboratory of G. N. Lewis at the University of California. In 1939 at the age of 33 Kapustinskii was elected Corresponding Member of the

Academy of Sciences of the USSR in the Division of Chemical Sciences. In 1941 he transferred to the Academy of Sciences USSR to work in the Institute of General and Inorganic Chemistry.

Kapustinskii's teaching activities started in 1930 in the department of physical chemistry of the Moscow higher Technical Institute. In the following years he became professor and director of the department of physical chemistry of Gor'kii State University (1933-1937), the Moscow Steel Institute (1937-1941), and Kazan State University (1941-1943). In 1943 he was elected professor in charge of the department of general and inorganic chemistry of the D. I. Mendeleev Moscow Chemico-technological Institute and he worked there till the end of his life. Kapustinskii was a remarkable orator and excellent lecturer. The numerous students and all who heard him will always remember his lectures and reports, which were brilliant both in content and form.

Kapustinskii's work covered an exceptionally wide range. He carried out a large number of investigations on many very important problems of chemistry. We should mention his work on the thermodynamics of metallurgical processes, crystal chemistry and especially the energetics of crystals, heats of formation of inorganic compounds, theoretical work on problems of the Periodic Law, geochemistry, solvation of ions in solutions, and the history of chemistry. The list of his works includes 350 titles. His best known work is that connected with problems of crystal chemistry. The equation he derived for the lattice energy of an ionic crystal (1933, 1943, and 1956) is given in all monographs and textbooks on crystal chemistry. In 1934 he introduced the very important concept of "thermochemical radii" of ions, which was particularly valuable in investigations of complex ions. In 1949 A. F. Kapustinskii proposed a new ionic constant, that of "crystallochemical electronegativity," which characterizes the electronic affinity of an ion in a crystal. In 1956 he derived a very simple equation which related such fundamental characteristics of ions in crystals as the radius, the charge, and the total number of electrons.

Kapustinskii's investigations throw light upon the most general and fundamental problems of chemistry. Thus, he was able to extend one of the most general laws of chemistry, Avogadro's Law, to cover the electronic structure of atoms and ions. In his investigations of the solvation of ions in solutions, Kapustinskii worked out a theory of quantitative characteristics of individual ions in solution and this made it possible for him to derive a single system for the entropy and radii of ions in aqueous solutions, as well as to propose an electronic mechanism for the hydration of ions in solutions.

His activity in the publishing field and popularization of science was very varied and fruitful. For almost twenty years he was a member and vice-chairman of the Editorial Board of the journal "Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk." In 1946 he became a member of the Main Editorial Board of the second edition of the Large Soviet Encyclopedia and headed the section on chemistry. He was editor of translated foreign monographs and textbooks. From 1957 Kapustinskii was chairman of the National Union of Soviet Historians of Chemistry. In 1960 he was elected honorary member of the Polish Chemical Society. For his outstanding contributions to the development of chemical science he was awarded the Order of the Red Labor Banner and medals. All those who knew the outstanding Soviet scientist and remarkable man Anatolii Fedorovich Kapustinskii, will always remember him.

DENSITY AND HEAT CAPACITY OF MIXED AQUEOUS SOLUTIONS OF LITHIUM AND POTASSIUM CHLORIDES AT 25°

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Nobody has determined the density and heat capacity of the system $\text{LiCl}-\text{KCl}-\text{H}_2\text{O}$. As regards other characteristics, the electrical conductivity [1], vapor pressure [2, 3], and solubility [4] are known. Meanwhile, the study of the properties of mixed solutions is of great practical interest as in general, it is necessary to deal with multicomponent rather than binary systems in practice. The investigations of these solutions is also of theoretical value as our ideas even on the simplest water-salt systems are inadequate. In this connection, it seemed interesting to study the additivity of the heat capacity and specific volume of the given system over a wide range of concentrations and examine the behavior of the electrolytes in each others presence. Together with this, it seemed possible to establish a relation between the properties studied and also to obtain new data on C_p of the individual solutions at high concentrations. The system $\text{LiCl}-\text{KCl}-\text{H}_2\text{O}$ was chosen because its components do not react chemically and include the highly hydrated lithium ion and the system itself is one of the simplest mixtures of chlorides of Group I elements.

EXPERIMENTAL

The solutions investigated were prepared by weight from the salts ("chemically pure" grades, recrystallized twice and subjected to quantitative spectral analysis) and triply distilled water; their concentrations were checked pycnometrically. The mixtures were prepared from two binary solutions of the same molal concentration with a salt ratio of 1 : 1.

The method of determining the density was based on that of Washburn and Smith [5], which was used previously by one of the authors and his co-workers [6-8]. The pycnometers were filled and emptied by means of vacuum [9]. The solutions were introduced into two pycnometers ($V = 60$ ml) in parallel and immersed in a thermostat ($25 \pm 0.005^\circ$). When thermal equilibrium had been established, the level of the liquid in the capillary was determined with a cathetometer (with an accuracy of ± 0.01 mm). The pycnometers were weighed with an accuracy of about 0.0001 g. The weights were corrected for air density [9]. The solution volume was determined by interpolation from calibration data. The pycnometers were calibrated with triply distilled water. The solution densities were related to the density of water, which was taken as unity at 4° . The accuracy of the density determinations was 0.001%.

The densities obtained are given in Tables 1, 2, and 3. These tables also give the calculated specific volumes (V_4^{25}), apparent and partial molal volumes of the salts (Φ_V , V_2), and also the relative partial molal volumes of water ($\bar{V}_1 - \bar{V}_1^\circ$). ** The values of Φ_V were determined from the formula:

$$\Phi_V = \frac{(mM + 1000) / d - 1000/d_0}{m} \quad (1)$$

where m is the molal concentration of the solution, M is the molecular weight of the salt, d is the solution density at 25° , and $d_0 = 0.99707$ is the density of water at 25° [10].

*Deceased.

**A. S. Kulyasov helped with the experiments and some of the calculations.

TABLE 1. Density, Specific Volume, and Apparent and Partial Molal Volumes of Aqueous Solutions of Lithium Chloride at 25°

Molal concentration, m	Density d_4^{25} , g/ml	Specific vol. v_4^{25} , ml/g	Apparent molal vol. Φ_V , ml/M	Partial molal vol. \bar{V}_0 , ml/M	Relative partial molal vol. of water ($\bar{V}_1 - \bar{V}_1^0$), ml/
0,5004	1,00915	0,99093	18,03	18,56	-0,0049
1,0030	1,02064	0,97978	18,44	19,20	-0,0154
1,4965	1,03142	0,96954	18,79	19,67	-0,0238
2,0111	1,04221	0,95950	19,08	20,06	-0,0355
2,5022	1,05215	0,95043	19,31	20,40	-0,0491
3,0051	1,06199	0,94163	19,52	20,70	-0,0639
3,6742	1,07461	0,93057	19,76	21,04	-0,0849
4,0480	1,08146	0,92468	19,87	21,22	-0,0985
4,5117	1,08975	0,91764	20,00	21,42	-0,1153

TABLE 2. Density, Specific Volume, and Apparent and Partial Molal Volumes of Aqueous Solutions of Potassium Chloride at 25°

Molal concentration, m	Density d_4^{25} , g/ml	Specific vol. v_4^{25} , ml/g	Apparent molal vol. Φ_V , ml/M	Partial molal vol. \bar{V}_0 , ml/M	Relative partial molal vol. of water ($\bar{V}_1 - \bar{V}_1^0$), ml/M
0,4976	1,01985	0,98054	28,10	28,95	-0,0077
0,9997	1,04153	0,96013	28,77	29,92	-0,0208
1,4961	1,06199	0,94163	29,28	30,63	-0,0364
2,0008	1,08173	0,92445	29,69	31,22	-0,0549
2,4861	1,09994	0,90914	30,06	31,69	-0,0731
3,0045	1,11862	0,89396	30,38	32,13	-0,0946
3,6741	1,14161	0,87596	30,75	32,62	-0,1239
3,9822	1,15178	0,86822	30,90	32,83	-0,1384
4,5090	1,16864	0,85570	31,16	33,14	-0,1621

TABLE 3. Density, Specific Volume, and Apparent and Partial Molal of Volumes of Mixed Aqueous Solutions of Lithium and Potassium Chlorides at 25°

Molal concentration			Density d_4^{25} , g/ml	Specific vol. v_4^{25} , ml/g	Apparent molal vol. Φ_V , ml/M	Partial molal vol. \bar{V}_2 , ml/M	Relative partial molal vol. of water ($\bar{V}_1 - \bar{V}_1^0$), ml/M
m LiCl	m KCl	total m					
0,2502	0,2488	0,4990	1,01454	0,98567	22,99	23,68	-0,0063
0,5015	0,4999	1,0014	1,03120	0,96974	23,53	24,47	-0,0169
0,7482	0,7491	1,4973	1,04700	0,95511	23,92	25,05	-0,0308
1,0056	1,0004	2,0060	1,06228	0,94137	24,32	25,53	-0,0438
1,2511	1,2431	2,4942	1,07652	0,92892	24,59	25,91	-0,0591
1,5026	1,5022	3,0048	1,09101	0,91658	24,86	26,29	-0,0777
1,8371	1,8371	3,6742	1,10900	0,90171	25,18	26,70	-0,1009
2,0240	1,9911	4,0151	1,11769	0,89470	25,24	26,89	-0,1191
2,2559	2,2545	4,5104	1,13100	0,88417	25,36	27,15	-0,1448

As the apparent molal volume gives the best linear relation when expressed as a function of the square root of the molal concentration (c) and not of \sqrt{m} , as Gucker showed [11], the following equation is most convenient for calculating \bar{V}_2 :

$$\bar{V}_2 = \Phi_V^0 + V_c \left[\frac{3000 - c \cdot \Phi_V^0}{2000 + c \cdot V_c \cdot \partial \Phi_V / \partial V_c} \right] \cdot \frac{\partial \Phi_V}{\partial V_c} \quad (2)$$

where Φ_V^0 is the apparent partial molal volume of the salt at infinite dilution.

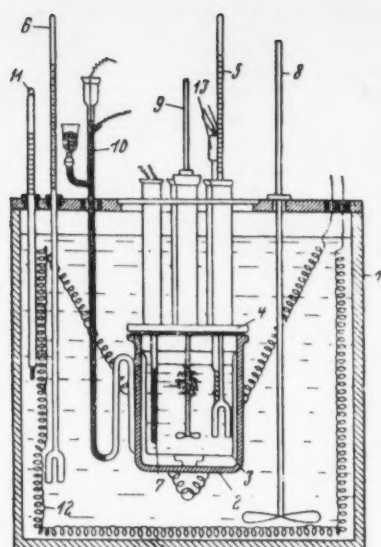


Fig. 1. Plan of calorimeter for measuring heat capacities: 1) calorimeter casing; 2,3) inner (nickel-plated metal) and outer (pyrex glass, capacity ~400 ml) calorimetric vessels; 4) nickel-plated metal lid with tubes for introducing instruments into the calorimeter; 5,6) calorimetric thermometers with scale divisions of 0.007°; 7) nichrome heating coil enclosed in an oil-filled, thin-walled glass ampoule; 8,9) stainless steel stirrers; 10) mercury-toluene thermoregulators; 11) thermometer with scale divisions of 0.2°; 12) thermostat heater; 13) standard platinum resistance thermometer for checking mercury thermometers.

The relative partial molal volumes of water ($\bar{V}_1 - \bar{V}_1^0$) were calculated from the equation:

$$(\bar{V}_1 - \bar{V}_1^0) = \frac{(mM + 1000)/d - m\bar{V}_2 - 1000/d_0}{55,508} \quad (3)$$

For the mixed solutions, Φ_V , \bar{V}_2 , and $(\bar{V}_1 - \bar{V}_1^0)$ were also calculated by means of equations 1, 2, and 3, but in this case, m and M corresponded to the total molal concentration and the mean molecular weight of the salts.*

The heat capacity of the solutions was determined in the adiabatic calorimeter illustrated in Fig. 1. The current strength was measured with the compensation apparatus we described previously [12]. The main features of the electric circuit of the resistance thermometer were the same as those used in a study of the heat capacity of cesium iodide solutions [13]. Adiabatic conditions were maintained by simultaneously supplying current to the thermostat and calorimeter heaters. A multipoint switch was used for synchronizing the switching on of the current and the calibrated seconds counter. Preliminary experiments showed that thermal equilibrium was established when the temperature of the calorimeter was 0.010–0.015° above the temperature of the thermostat. In practice it was permissible to have a somewhat greater difference (0.025°). In this case the correction for heat exchange was so small that it lay within the limits of experimental error. To avoid evaporation, 13.00 g of carefully purified oil was added to the calorimetric liquid each time; the solution volume was kept constant. The error in the determination of C_p was 0.05% on an average. Table 4 gives the specific heat capacities (C) of the solutions. The apparent and partial molal heat capacities were calculated from well-known formulas [15].

The thermodynamic characteristics obtained were examined from the point of view of additivity. The calculations were carried out with the formula of D'Ans and Tollert [16, 17].

All the volume characteristics showed deviation from additivity; the heat capacities showed some deviations with concentrated solutions, but they were very small and irregular.

Figures 2, 3, and 4 show the concentration dependences of the apparent and partial molal values.

In addition to this, we calculated the apparent molal values for each electrolyte in the mixture (Table 5) by the equation proposed by Wirth [18]:

$$\Phi_1 = \frac{(mM + 1000)/d - (1000/d_0 + m_2\Phi_2)}{m_1} \quad (4)$$

where Φ_1 is the apparent molal volume of the 1st salt in the mixed solution, containing m_1 and m_2 moles of solutes per 1000 g of H_2O and Φ_2 is the apparent volume of the 2nd salt in a binary solution at a concentration of m_2 .

However, in this case, as in Wirth's work, no allowance was made for the change in the apparent molal volume (Φ_2) of one salt in the presence of the other. Attempts to eliminate this deficiency by combining equation (4) with a number of others were unsuccessful. Despite this, these calculations are of interest in our opinion as they give a qualitative idea of the behavior of electrolytes in each others presence.

* $M = M_{LiCl} x_{LiCl} + M_{KCl}$, where x is the mole fraction of the salt in the mixture.

TABLE 4. Specific Heat Capacities of Aqueous Solutions of Lithium and Potassium Chlorides at 25°

LiCl Solution		KCl solution		Mixed solution			
molal concentration, m	specific heat capacity C_p , cal/g.deg	molal concentration, m	specific heat capacity C_p , cal/g.deg	m_{LiCl}	m_{KCl}	total concentration, m	specific heat capacity C_p , cal/g.deg
0,499	0,9718*	0,498	0,9520	0,250	0,249	0,499	0,9615
0,998	0,9487	1,000	0,9116	0,499	0,500	0,999	0,9302
1,506	0,9257	1,492	0,8771	0,753	0,746	1,499	0,9006
2,011	0,9068	2,001	0,8442	1,006	1,000	2,006	0,8750
2,502	0,8876	2,486	0,8176	1,251	1,243	2,494	0,8513
3,005	0,8686	3,004	0,7891	1,502	1,502	3,004	0,8283
3,674	0,8450	3,674	0,7590	1,837	1,837	3,674	0,8014
4,048	0,8344	3,982	0,7450	2,024	1,991	4,015	0,7890
4,512	0,8196	4,509	0,7224	2,256	2,254	4,510	0,7697

*Corrected to 15° calories; data of Cucker and Schminke [14].

TABLE 5. Apparent Molal Volumes and Heat Capacities of LiCl and KCl in Mixed Aqueous Solutions at 25°

Total molal concentration, m	Apparent M vol. of LiCl in mixture, $\Phi_V(LiCl)$	Apparent M vol. of KCl in mixture, $\Phi_V(KCl)$	Apparent M heat capacity of LiCl in mixture, $\Phi_C(LiCl)$	Apparent M heat capacity of KCl in mixture, $\Phi_C(KCl)$
0,4990	18,30	28,26	-10,0	-20,5
1,0014	18,86	29,03	-5,9	-15,2
1,4973	19,33	29,55	-5,2	-13,7
2,0060	19,87	30,21	-2,3	-10,1
2,4942	20,17	30,60	-1,2	-8,7
3,0048	20,44	30,93	-1,0	-7,3
3,6742	20,80	31,39	+1,0	-5,1
4,0151	20,88	31,53	+1,6	-4,2
4,5104	20,92	31,57	+1,5	-4,0

DISCUSSION OF EXPERIMENTAL RESULTS

Comparison of the concentration dependences of the heat capacities and volume properties shows that they are relatively simple and analogous. This indicates that there is an inherent relation between them as has been pointed out already by Thomsen et al., [19, 20]. The relation of C_p^{25} to V_4^{25} for the system we studied is close to linear. Below we give empirical equations which make it possible to calculate the more difficultly determinable values of C_p from known specific volumes with an accuracy of 0.1-0.2%.

$$LiCl - H_2O : C_p^{25} = (2,0676 V_4^{25} - 1,0780) \pm 0,0006 \quad (5)$$

$$KCl - H_2O : C_p^{25} = (1,849 V_4^{25} - 0,862) \pm 0,002 \quad (6)$$

$$LiCl - KCl - H_2O : C_p^{25} = (1,8998 V_4^{25} - 0,9124) \pm 0,0011 \quad (7)$$

The coefficients in the equations were found by the method of least squares. An examination of the relations of the apparent and partial values to the square root of the concentration shows that they obey the Masson-Randall-Rossini rule and nonlinearity of the values of Φ_C and \bar{C}_{p2} is observed only with concentrated solutions. For binary solutions, the apparent molal values at infinite dilution (Φ_V^∞ and Φ_C^∞) and also the slopes of the lines agree well with highly accurate literature data [14, 15, 21]. In the case of mixed solutions, the apparent molal volumes and heat capacities may be expressed by the equations:

$$\Phi_V = 21,72 + 1,870 \sqrt{c} \quad (8)$$

$$\Phi_C = -21,5 + 7,78 \sqrt{m} \quad (9)$$

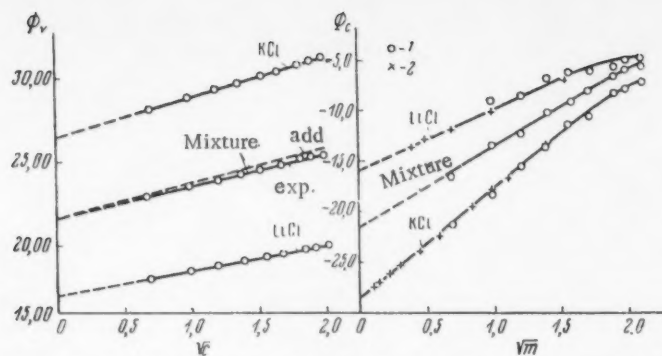


Fig. 2. Relation of Φ_V and Φ_C to the square root of the concentration at 25°: 1) Our data; 2) data of Randall and Rossini [21] for KCl and of Cucker and Schminke [14] for LiCl.

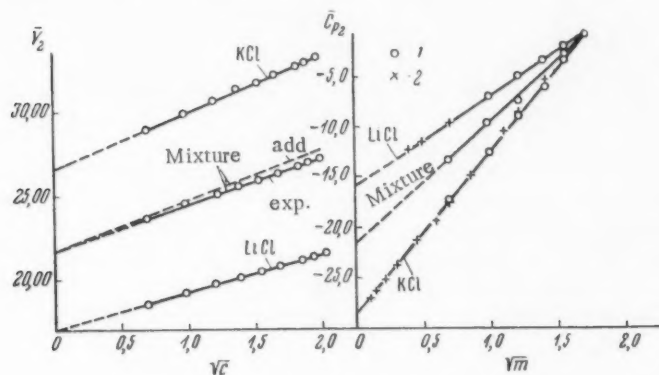


Fig. 3. Relation of \bar{V}_2 and \bar{C}_{P2} to the square root of the concentration at 25°: 1) Our data; 2) data of Randall and Rossini [21] for KCl and of Cucker and Schminke [14] for LiCl.

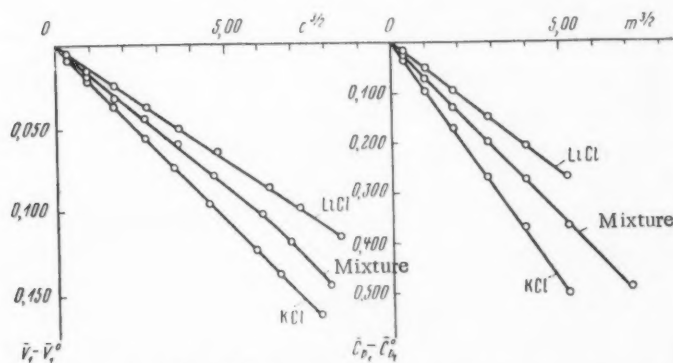


Fig. 4. Relation $(V_1 - V_1^0)$ and $(\bar{C}_{P1} - \bar{C}_{P1}^0)$ to the concentration at 25°.*

*The values of \bar{C}_{P2} and $(\bar{C}_{P1} - \bar{C}_{P1}^0)$ for high concentrations, where the Masson-Randall-Rossini rule does not hold, are not given because of the unreliability of graphical differentiation.

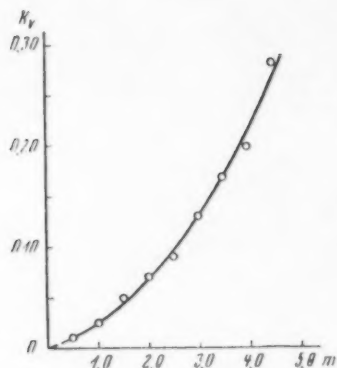


Fig. 5. Relation of K_V to concentration at 25°.

In its turn, this makes it possible to find the relation of the integral values (C_p^{25} and V_4^{25}) to the concentration:

$$V_4^{25} = \frac{m(21.72 + 1.870 \sqrt{c}) + 1002.94}{mM + 1000} \quad (10)$$

$$C_p^{25} = \frac{m(-21.5 + 7.78 \sqrt{m}) + 997.9}{mM + 1000} \quad (11)$$

From equations (8) and (9) it follows that the slope of a plot of the thermal capacity is much greater than that of the volume properties. This sharp quantitative difference may be connected with a greater effect of the ions on C of water than on its volume rather than a different change in the heat capacities and volumes of the electrolytes themselves in solution [20]. This is also confirmed by Fig. 4. Comparison of the experimental specific volumes (V_{exp}) of the mixture with the additive values (V_{add}) shows a certain "depression," which we will subsequently call the "contraction coefficient":

$$K_V = \frac{V_{\text{add}} - V_{\text{exp}}}{V_{\text{add}}} \cdot 100\% \quad (12)$$

The relation $K_V = f(m)$ is given in Fig. 5, which shows a regular increase in the "depression" with an increase in m . This may be explained by the fact that during mixing there is partial redistribution of the effect of the ions on water. Thus, the Li^+ ion, which has a smaller radius ($r_{\text{Li}^+} = 0.78 \text{ \AA}$ and $r_{\text{K}^+} = 1.33 \text{ \AA}$) and a stronger electrostatic field, extends its effect in the mixture to part of the water that was previously in the force field of the K^+ ion. In its turn, this evidently leads to greater contraction of the water dipoles close to the ions and consequently a reduction in the volume of the whole solution. On the other hand, the excess of the values of Φ_V calculated by Wirth's equation (4) over those in individual solutions at the same ionic strength indicates the natural interaction of the ions, increasing with an increase in the electrolyte concentration. As a result of this interaction there may arise a force which prevents the depression somewhat, i.e., the force field of the ions is weakened and the effect of the ions on water decreases.

Thus, the behavior of ions in mixed solutions, as in simple solutions, is composed of different types of complex interaction. It is not possible to calculate them separately. Therefore, it is expedient to approach the problem from the other direction, namely, to determine the predominating factors on the basis of experimental data. The present work shows that in the change in volume in the system $\text{LiCl}-\text{KCl}-\text{K}_2\text{O}$, the ion-dipole interaction apparently has the decisive influence.

SUMMARY

1. The heat capacities and densities of the water-salt system $\text{LiCl}-\text{KCl}-\text{H}_2\text{O}$ were determined for the first time and also the heat capacities of binary concentrated solutions at 25°.
2. There was a linear relation between the heat capacity and volume for all the solutions investigated and this may be used for practical purposes.
3. A deviation of the specific volumes from additivity was found; an attempt was made to explain this phenomenon by an ion-dipole interaction.
4. In mixed solutions there is an increase in apparent values in comparison with binary solutions and this may be the result of an interionic interaction.

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SYSTEMS WITH CONCENTRATED HYDROGEN PEROXIDE

COMMUNICATION 22. THERMAL ANALYSIS OF COPPER PEROXIDES

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In a study of the system $\text{Cu}(\text{OH})_2\text{-H}_2\text{O}_2\text{-H}_2\text{O}$ over the temperature range of -36 to 20° [1], it was established that the two following solid peroxide phases are present in the system: $\text{CuO}_2 \cdot \text{H}_2\text{O}$ and $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$. The compound $\text{CuO}_2 \cdot \text{H}_2\text{O}$ was known previously [2-7], while the compound $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ was obtained for the first time by us. A number of authors [2, 4, 5] have attempted to obtain anhydrous copper peroxide by dehydration of $\text{CuO}_2 \cdot \text{H}_2\text{O}$, but it was impossible to obtain CuO_2 of adequate purity because of the decomposition that occurs in parallel. The new compound $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ obtained was found to be more suitable in this respect and made possible a much closer approach to the preparation of anhydrous CuO_2 .

Products from $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ of maximum dehydration, which contained more than 10-11% of active oxygen and included anhydrous CuO_2 , were black crystalline powders that were stable during storage and had sharply expressed oxidizing properties.

The reaction of these powders with solutions of Fe^{2+} , Mn^{2+} , and Cr^{3+} salts produced rapid oxidation and the formation of Fe^{3+} , Mn^{4+} , and Cr^{6+} compounds. Oxalic acid was oxidized rapidly to CO_2 . The acidification of an aqueous suspension of CuO_2 with sulfuric acid formed H_2O_2 , which could be titrated with KMnO_4 . In this respect,

CuO_2 is a typical peroxide compound $\text{Cu} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array}$

In the present communication we present data from thermal investigations of the solid peroxide phases found on studying the ternary system and also the heating curve of the starting hydroxide $\text{Cu}(\text{OH})_2$, data on the dehydration of "residues" and x-ray diffraction patterns of Cu_2O_3 and CuO_2 .

Thermal Analysis of Copper Peroxides

All the heating curves of the solid phases given were plotted on a Kurnakov recording pyrometer in the differential form with a heating rate of $\sim 6^\circ$ per min.

CuO_2 . Figure 1 gives heating curves of CuO_2 in parallel with the curve of active oxygen liberation. The main and differential curves clearly showed an exothermal effect at 110° , which was associated with decomposition of CuO_2 according to the equation $2\text{CuO}_2 \rightarrow 2\text{CuO} + \text{O}_2$. The liberation of oxygen began much earlier, but accelerated sharply at 110° . The presence of the exothermal effect was characteristic of CuO_2 .

$\text{Cu}(\text{OH})_2$. The heating curves of $\text{Cu}(\text{OH})_2$ also had a comparatively simple form (Fig. 2) with the differential curve showing an endothermal effect at 100° and the main curve showing a clear plateau at the same temperature. In this case there was simple conversion of $\text{Cu}(\text{OH})_2$ to CuO according to the equation $\text{Cu}(\text{OH})_2 \rightarrow \text{CuO} + \text{H}_2\text{O}$, with a corresponding clear change from blue to black. The differential curves of CuO_2 and $\text{Cu}(\text{OH})_2$ were antipodes.

$\text{CuO}_2 \cdot \text{H}_2\text{O}$. The analysis of the starting material was as follows: CuO 70.06%, act. O_2 14.09%, and H_2O 15.85%. The differential heating curve (Fig. 3) combined the characteristics of the heating curves of CuO_2 (an exothermal effect at 90°) and $\text{Cu}(\text{OH})_2$ (an endothermal effect at 100°). The decomposition of the compound $\text{CuO}_2 \cdot \text{H}_2\text{O}$ with the liberation of active oxygen proceeded at a high rate at 90° and above and when the process was complete, all the water had been eliminated by the reactions: $2\text{CuO}_2 \cdot \text{H}_2\text{O} \rightarrow 2\text{Cu}(\text{OH})_2 + \text{O}_2$, $2\text{Cu}(\text{OH})_2 \rightarrow 2\text{CuO} + \text{H}_2\text{O}$.

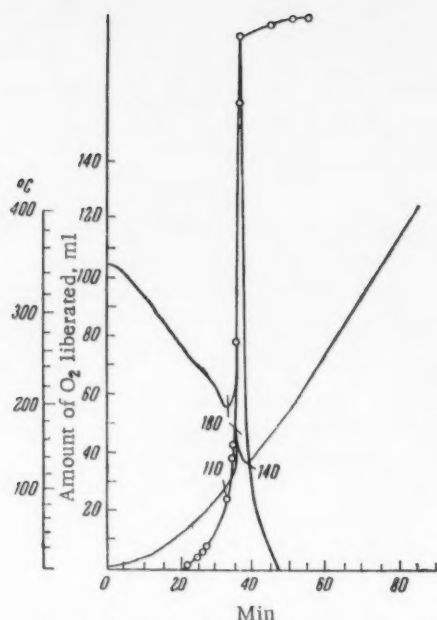


Fig. 1. Heating and active oxygen liberation curves of CuO_2 .

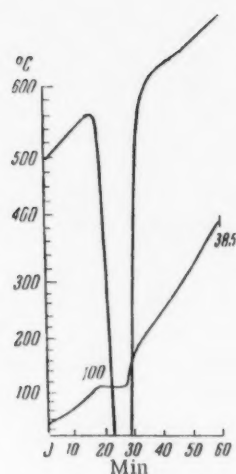


Fig. 2. Heating curve of Cu(OH)_2 .

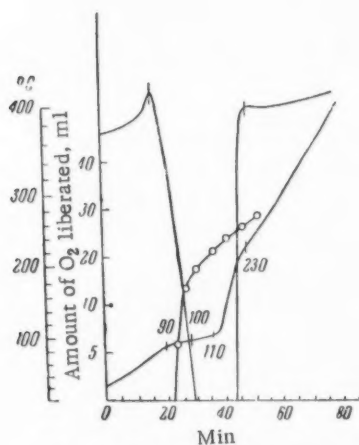


Fig. 3. Heating and active oxygen liberation curves of $\text{CuO}_2 \cdot \text{H}_2\text{O}$.

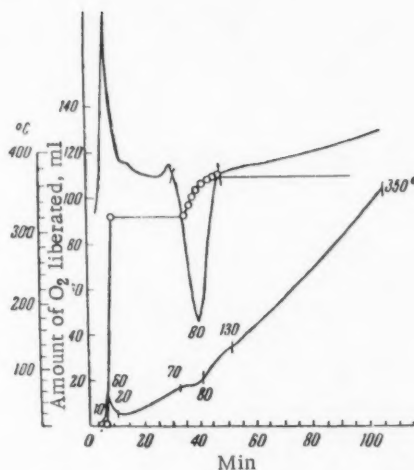


Fig. 4. Heating and active oxygen liberation curves of $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$.

$\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$. The analysis of this product was as follows: CuO 53.92%, act. O_2 21.68% and H_2O 24.40%. The heating curves plotted (Fig. 4) were more complex. In addition to the thermal effects characteristic of the compound $\text{CuO}_2 \cdot \text{H}_2\text{O}$, there was also a sharply expressed exothermal effect at 20° , which was associated with the unstable hydrogen peroxide of crystallization. Such thermal effects are characteristic of many perhydrate compounds. The second exothermal effect at 70° was also small in size due to the fact that during the decomposition of H_2O_2 , active oxygen was also lost from CuO_2 . The dehydration and conversion of the starting compound to CuO began at 70° with parallel completion of the liberation of active oxygen. The active oxygen liberation curve given in Fig. 4 confirms the occurrence of the conversions $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O} \rightarrow \text{CuO}_2 \cdot \text{H}_2\text{O} \rightarrow \text{CuO}$.

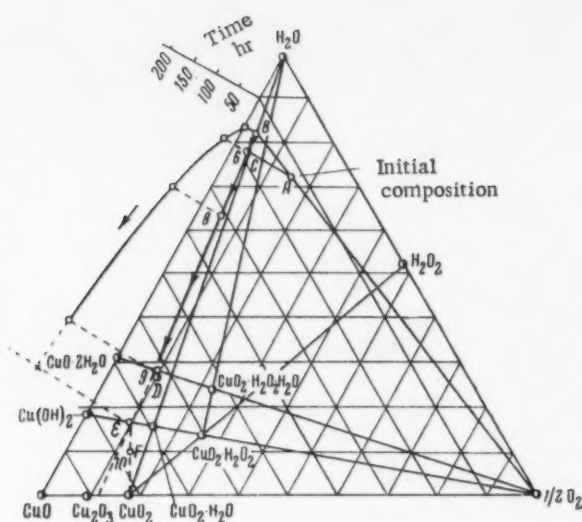


Fig. 5. Diagram of the change in composition of the "residue" $\text{CuO}_2 \cdot \text{H}_2\text{O}$ on dehydration.

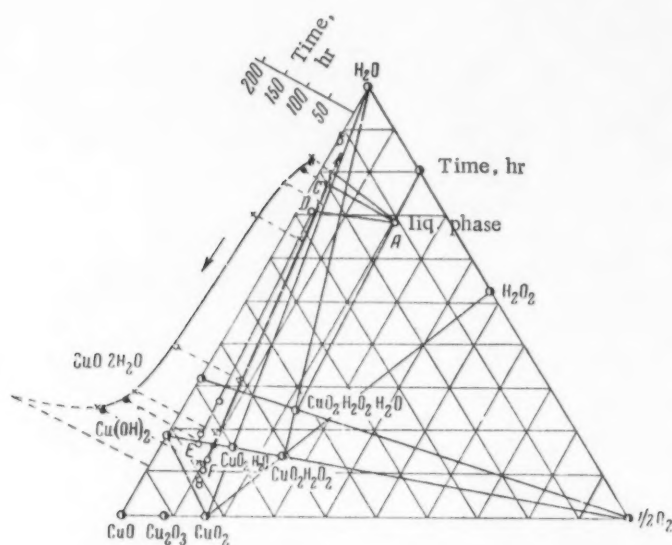


Fig. 6. Diagram of the change in composition of the "residue" $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ on dehydration.

Thus, of all the copper peroxides examined, anhydrous copper peroxide CuO_2 is the most stable thermally. The hydrated form $\text{CuO}_2 \cdot \text{H}_2\text{O}$ is much less stable and the least stable compound is $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$. A valuable property of the latter is the fact that under certain dehydration conditions, the presence of active oxygen in the form of bound H_2O_2 promotes the formation of CuO_2 of higher quality and offers the possibility of its extensive synthesis and perhaps its use as an active oxygen-containing catalyst.

Dehydration of the "Residues" $\text{CuO}_2 \cdot \text{H}_2\text{O}$ and $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$

The compounds $\text{CuO}_2 \cdot \text{H}_2\text{O}$ and $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ prepared by the reactions of copper hydroxide and hydrogen peroxide always contained a considerable amount of aqueous solutions of hydrogen peroxide. It was extremely difficult to separate the mother solutions with the solid phases in a highly disperse state. Therefore, the drying of these

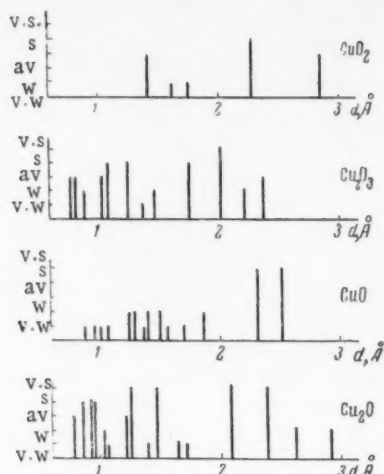


Fig. 7. Diagram comparing the relation of the interplanar distances and line intensities on x-ray diffraction patterns of copper oxides.

peroxide in the solution) and then along BD there was a loss of water with a gradual increase in the loss of active oxygen. The process occurred slowly and the composition reached after 120 hr, is represented by the point D and point E, which corresponds to the mechanical mixture $\text{CuO}_2 \cdot \text{H}_2\text{O} + \text{Cu}(\text{OH})_2$.

Figure 6 shows that the composition of the "wet residue" A actually corresponds to the solid phase $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$. Depending on the drying conditions, (over H_2SO_4 at 0° , P_2O_5 at 0° , and P_2O_5 at 27°), the compositions reached after 24 hr are represented by the points B, C, and D, with the process occurring more rapidly at 27° . The subsequent change in the compositions was similar to the previous one and after 6 days (only in the case of drying at 27° over P_2O_5), the composition obtained (point F) was a mechanical mixture of $\text{Cu}(\text{OH})_2 + \text{CuO}_2 \cdot \text{H}_2\text{O} + \text{CuO}_2$.

With the use of small samples of ~ 0.5 g, in this case it was easy to obtain products of high stability with the composition: CuO 81.6%, O_2 act. 11.90% and H_2O 6.5% (CuO_2 contains 83.26% of CuO and 16.74% of O_2 act.), containing free CuO_2 . Therefore, to obtain anhydrous copper peroxide CuO_2 of sufficient quality, it was necessary to use rapid vacuum drying and $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ as the starting material.

Qualitative X-ray Phase Analysis of Oxygen Compounds of Copper

The copper peroxide with the approximate composition CuO_2 , which was obtained by dehydration of $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$, was compared with other known oxygen compounds of copper, namely, Cu_2O , CuO , and Cu_2O_3 , by means of Debye-Scherrer x-ray diffraction patterns. We prepared the compound Cu_2O_3 by anode-oxidation of metallic copper. The patterns were photographed on a URS-70 apparatus, using copper radiation with a nickel filter, by A. A. Kanishcheva and A. N. Zimina.

Figure 7 gives comparative diagrams of the relation of the interplanar distances and line intensities for copper oxides. The x-ray diffraction line at 2.84 Å for CuO_2 is characteristic of the latter and confirms its presence. Tables 1 and 2 give the data we obtained from x-ray diffraction patterns of Cu_2O_3 and CuO_2 .

TABLE 1. Data from X-ray Diffraction Patterns of Cu_2O_3

Intensity	2I	t	θ°	d, Å	Intensity	2I	t	θ°	d, Å
Average	37,8	18,9	18°42'	2,40	Strong	75,8	37,9	37°31'	1,26
Weak	40,2	20,1	20°	2,25	Strong	91,6	45,8	45°18'	1,08
V. strong	44,8	22,4	22°10'	2,04	Average	97,0	48,5	48°	1,035
Strong	52,0	26,0	25°46'	1,77	Weak	119,0	59,5	58°54'	0,898
Weak	63,0	31,5	31°12'	1,48	Average	138,6	69,3	68°48'	0,826
V. weak	67,8	33,9	33°32'	1,40	Average	147,0	73,5	72°43'	0,806

TABLE 2. Data from X-ray Diffraction Patterns of CuO_2

Intensity	2θ	θ	θ°	$d, \text{\AA}$	Intensity	2θ	θ	θ°	$d, \text{\AA}$
Average	32,9	16,0	15'42"	2,84	Weak	57,4	28,7	28'24"	1,62
Strong	39,8	19,9	19'42"	2,28	Average	66,6	33,3	32'58"	1,41
Weak	52,6	26,3	26'02"	1,75					

DISCUSSION OF THE RESULTS

Thermal analysis and dehydration over phosphorus pentoxide of the solid peroxide phases found in the system $\text{Cu}(\text{OH})_2 - \text{H}_2\text{O}_2 - \text{H}_2\text{O}$ showed that the dehydration is accompanied by the decomposition of these compounds and the initiator of the decomposition is H_2O_2 in the liquid phase absorbed by the residues. Data from the investigation of the solid phases $\text{CuO}_2 \cdot \text{H}_2\text{O}$ and $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ give adequate grounds for regarding these compounds as hydroperoxides with the structures $(\text{Cu}(\text{OOH})(\text{OH}))$ and $(\text{Cu}(\text{OOH})(\text{OH})) \cdot \text{H}_2\text{O}_2$.

In this case it is readily seen why there is difficulty in obtaining anhydrous CuO_2 with the theoretical content of active O_2 (16.7%) from $(\text{Cu}(\text{OOH})(\text{OH}))$. By careful drying at low temperatures it was possible to obtain a product with 11.9% of active oxygen and containing CuO_2 , as was confirmed by the differential heating curve and the x-ray diffraction pattern.

SUMMARY

1. The solid phases $\text{Cu}(\text{OH})_2$, $\text{CuO}_2 \cdot \text{H}_2\text{O}$, and $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$, found in a study of the ternary system, and also CuO_2 that was synthesized were examined by thermal analysis and active oxygen liberation curves were plotted.
2. The sequence of the processes in the thermal decomposition of all the compounds given was studied.
3. Anhydrous CuO_2 is most stable and decomposes at 110-120° to form CuO and O_2 .
4. The formation of CuO_2 by dehydration of $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ was confirmed by thermal analysis data and Debye-Scherrer x-ray diffraction patterns.
5. The compounds $\text{CuO}_2 \cdot \text{H}_2\text{O}$ and $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ should be regarded as hydroperoxides of the type $(\text{Cu}(\text{OOH})(\text{OH}))$ and $(\text{Cu}(\text{OOH})(\text{OH})) \cdot \text{H}_2\text{O}_2$.

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INVESTIGATION OF CATALYTIC CONVERSIONS
OF ISOPROPANOL AND CYCLIC HYDROCARBONS
ON TITANIUM DIOXIDE (ANATASE) BY MEANS
OF A DIFFERENTIAL THERMOCOUPLE

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The investigation of such problems as the change in activity of a catalyst during an experiment and its regeneration, the activity of different catalysts in the same reaction, carbon formation on a catalyst, and finally reaction equilibrium and kinetics is facilitated by the use of a differential thermocouple [1-3]. A differential thermocouple makes it possible to measure heat effects of processes occurring on a catalyst and hence study all the factors affecting the rate of these processes. By the "heat effect of reaction" we mean the heat liberated during the given process, which is a measure of the rate of the catalytic reaction under definite conditions. The great advantage of the method is the fact that it makes it possible to determine rapid changes in activity and selectivity occurring in the first 10-20 min after the beginning of an experiment (until stationary conditions are established).

In our work, a differential thermocouple (chromel-copel) was used for studying the dehydrogenation and dehydration of isopropanol and irreversible catalytic reactions of hydrocarbons (cyclohexane, cyclohexene, and 1,4-cyclohexadiene) on one modification of titanium dioxide (anatase).

EXPERIMENTAL

The differential thermocouple had 20 junctions—10 junctions on each side of the mica sheet to which it was fixed with all 20 junctions lying on one half of the sheet; the total length of the sheet was 50 mm, the width corresponded to the internal diameter of the quartz tube, and the thickness was 1 mm. The catalyst was arranged in the tube with the differential thermocouple as shown in Fig. 1. The sheet was arranged in the reactor in such a way that the substance introduced first encountered the half of it that bore the junctions. The readings of the differential thermocouple could be distorted with the sheet the other way around. A normal thermocouple (chromel-copel) was fixed to the same sheet. The ends of the two thermocouples lead out from the catalyst tube through openings at its ends; the places where the wires emerged were covered with water glass. The emf of the thermocouple was recorded continuously with an EPP-09 potentiometer with the pointer in the center of the scale so that it was possible to record both endo- and exothermal effects.

Kinetic experiments were carried out in a reactor of the flow type [4, 5]. The activation energy was calculated from the temperature dependence of the m-volume of one of the gaseous reaction products formed in unit time (ml/min) since the degree of conversion did not exceed 30%. The temperature was maintained with an accuracy of $\pm 0.5^\circ$. The substance was introduced automatically from a glass syringe with a universal pulsed reducing gear [6]. The liberation rate and amount of gaseous reaction products were measured and recorded with a GSP-10 automatic gas meter. An example of a record is given in Fig. 2, which shows that the gas liberation rate was constant during the whole of the experiment. The volume of the gaseous products was reduced to n.p.t. The gas was analyzed on an automatic bubble gas analyzer [7]. The amount of carbonaceous deposits (coke) on the catalyst was determined by combustion of them. The starting material and its conversion products were first removed from the reactor and catalyst surface with a stream of oxygen-free nitrogen. Air was then blown through the catalyst at a constant rate and a temperature 40-50° above the experimental temperature. The water formed was absorbed with silica gel and the CO₂ with ascarite in a U-tube; the amount of combustion was determined from the increase in weight of the latter.

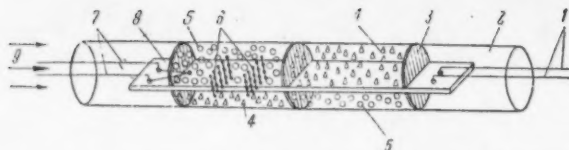


Fig. 1. Arrangement of catalyst in tube with differential thermocouple. 1) Differential thermocouple leads; 2) catalyst tube; 3) glass wool; 4) lumps of quartz; 5) catalyst; 6) differential thermocouple junctions; 7) leads of normal thermocouple; 8) mica plate to which differential thermocouple was fixed; 9) direction of flow of substance.

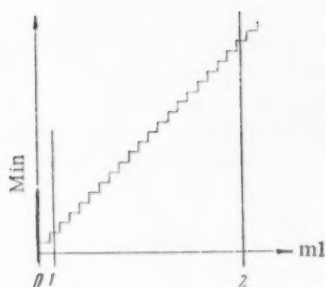


Fig. 2. Recording of gas evolution rate on GSP-10 gas meter. 0) Moment substance admitted to catalyst tube; 1) beginning of recording of gas liberated during reaction; 2) end of recording. The interval between 1 and 2 was 20 min.

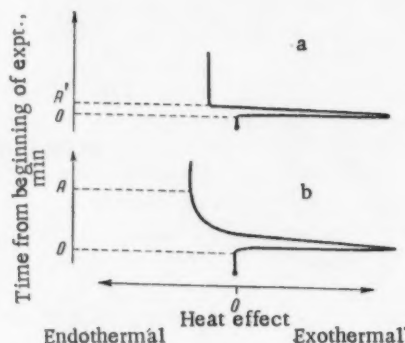


Fig. 3. Comparison of records of the differential heat effect of the reaction of isopropanol on TiO_2 and Cr_2O_3 catalysts: a) differential heat effect of the reaction on titanium dioxide. The intercept OA corresponds to 20 min; b) differential heat effect of the reaction on chromium oxide. The intercept OA corresponds to 1-2 min.

The catalyst was prepared by hydrolysis of titanium tetrachloride with distilled water at room temperature, washing the hydroxide obtained free from Cl^- (with distilled water at 50° for 50 hr), drying it at 110° (6 hr), and dehydrating the hydroxide with a gradual rise in temperature to 580° over 24 hr. X-ray structural analysis showed that anatase was formed.

Constants of starting materials: isopropanol, b.p. 82.2° (747 mm); d_4^{20} 0.7856; n_D^{20} 1.3777; cyclohexane, b.p. 80.0° (751 mm); d_4^{20} 0.7782; n_D^{20} 1.4266; cyclohexene, b.p. 82.5° (756 mm); d_4^{20} 0.8093; n_D^{20} 1.4455; 1,4-cyclohexadiene, b.p. $86.5-88^\circ$ (751.5 mm); d_4^{20} 0.8480; n_D^{20} 1.4728.

Dehydrogenation and dehydration of isopropanol. In a study of the conversion of isopropanol on TiO_2 with the aid of the differential thermocouple, we found a sharp change in the heat effect of the process in the first 15-20 min of the experiment (Table 1, Fig. 3, a). It was found (Fig. 3, a) that after the normal brief exothermal effect, which was caused by the initial adsorption of the starting substance, there was a gradual (over a period of 15-20 min) increase (in absolute value) in the endothermal effect of the catalytic process itself. In addition, the over-all rate of conversion of the alcohol remained unchanged during the whole of the experiment (Fig. 2). This change in the heat effect of the process with the total activity of the catalyst remaining constant indicates that the rate of one of the reactions of the alcohol decreased, while the rate of the other increased to an equal extent. Analysis of samples of the gaseous reaction products during the experiment showed (Table 1) that in the first 7-8 min, there was practically only dehydrogenation, then the two reactions occurred together with the ratio of the dehydrogenation rate to the dehydration rate gradually decreasing, and after 15-20 min from the beginning of the experiment, only dehydration

TABLE 1. Change in Gas Composition and Magnitude of Heat Effect during Conversion of Isopropanol on TiO_2

Time from beginning of expt., min	ΔH^*	Gas composition	
		C_3H_6	H
8-10	5-11	43.8	54.5
15	12-15	61.7	38.2
20	15-16	72.5	26.8

* ΔH is the heat effect of the reaction in scale divisions of the potentiometer.

occurred. Unregenerated, carbonized catalyst, treated with a stream of oxygen-free nitrogen, produced only dehydration of the alcohol from the very beginning and the heat effect of the process did not change during the whole of the experiment.

From a comparison of the readings of the differential thermocouple, the results of analysis of the reaction products during the experiment, and the degree of carbonization of the surface it follows that there is a symbatic relation between the change in the ratio of the isopropanol dehydrogenation and dehydration rates and the carbonization of the TiO_2 . Although carbon deposition on catalysts during a reaction has been known for a long time [8-12], there are no facts in the literature analogous to those described above. In all probability, the change in the selectivity of TiO_2 with the over-all activity remaining constant is connected with carbonization of the surface, which changes the nature of the active centers, while the number of centers and their activity apparently does not change appreciably.

At the same time, we were able to show (Fig. 3, b) that carbonization of a Cr_2O_3 surface does not affect the activity and selectivity of Cr_2O_3 in the dehydrogenation and dehydration of isopropanol; the ratio of the rates of these reactions remained unchanged during the whole of the experiment (1-2 hr) and the magnitude of the heat effect of the process did not change.

As follows from Tables 2-4, carbon deposition on TiO_2 affects the selectivity of the catalyst by changing the activation energies and preexponential factors K_0 of isopropanol dehydrogenation and dehydration. Thus, the activation energy of dehydrogenation on uncarbonized TiO_2 is 2.9 kcal/mole greater than on partly carbonized TiO_2 ; in addition, carbon deposition leads to complete suppression of this reaction. In addition, carbon deposition apparently has some effect on the energy of neighboring dehydrogenation centers which are still uncarbonized. It is interesting to note that the value of K_0 of dehydrogenation, which is proportional to the number of active dehydrogenation centers, is greater on uncarbonized TiO_2 than on partly carbonized TiO_2 .

With the aid of the differential thermocouple, we rapidly found conditions for regeneration of TiO_2 : after each experiment with alcohol, the carbonaceous film was removed by passing a stream of air for 20-30 min at a temperature 40-50° above the experimental temperature. The end of regeneration was indicated by the reading of the EPP-0.9 potentiometer: a zero reading corresponded to complete removal of coke. It was shown that combustion of the carbonaceous deposits proceeded gradually: only the surface film of the coke was removed at the experimental temperature, but with a rise in temperature of 40-50°, the remaining coke lying in the pores was burned. The experiments were always reproducible after the TiO_2 had been regenerated in this way.

Dehydrogenation of cyclohexane. In the present work it was shown that during the dehydrogenation of cyclohexane on TiO_2 , there is a small increase in activity at first with an increase in the carbonization of the surface, but with complete carbonization, there is a certain decrease in activity (Table 5). The reaction was studied on completely carbonized TiO_2 , where the carbonaceous film was not removed from the catalyst even by regeneration (the regeneration was carried out with a stream of air at the experimental temperature for 30 min), and on incompletely carbonized TiO_2 . In the latter case, the regeneration was the same as in the case of isopropanol conversions. In both

TABLE 2. Dehydrogenation of Isopropanol on Uncarbonized TiO_2 (catalyst volume 6.4 ml, weight 4.4 g, bed length 20 mm, input rate 0.294 ml/min)
 $\epsilon_{\text{H}_2} = 11900 \text{ cal/mole}$; $K_0 \text{ mean} = 1.9 \cdot 10^{-5}$

Temp. °C	m_{H_2} , ml per min of catalyst	$\lg K_0$	$\frac{\epsilon}{\lg K_0} 10^{-3}$
266	2,94	5,31	2,24
	2,56	5,23	2,28
282	4,35	5,33	2,24
	3,97	5,29	2,25
294	5,2	5,30	2,25
	4,95	5,25	2,26
310	6,87	5,30	2,25
	6,22	5,25	2,26
Mean		5,28	2,25

TABLE 3. Dehydrogenation and Dehydration of Isopropanol on Partly Carbonized TiO₂ (catalyst volume 6.4 ml, weight 4.4 g, bed length 20 mm, input rate 0.294 ml/min) $\epsilon_{H_2} = 9000$ cal/mole; K_0 mean = $1.02 \cdot 10^4$ $\epsilon_{H_2O} = 24400$ cal/mole; K_0 mean = $4.5 \cdot 10^9$

Temp. °C	m_{gas} , ml/min	Dehydrogenation			Dehydration			Gas analysis, %	
		m_{H_2} , ml/ min · ml of catalyst	$lg K_0$	$\frac{\epsilon}{lg K_0} \cdot 10^{-3}$	$m_{C_3H_6}$, ml/ per min · ml of catalyst	$lg K_0$	$\frac{\epsilon}{lg K_0} \cdot 10^{-3}$	C ₂ H ₄	H ₂
266	18,8	2,28	4,02	2,24	0,61	9,68	2,52	20,7	77,6
282	27,8	2,94	4,02	2,24	1,39	9,74	2,50	32,0	68,0
294	33,4	3,25	3,97	2,27	1,95	9,69	2,52	37,6	62,4
310	44,0	4,35	4,01	2,24	2,50	9,55	2,56	36,8	63,2
		Mean	4,01	2,24		9,65	2,53		

TABLE 4. Dehydration of Isopropanol on Completely Carbonized TiO₂ (catalyst volume 10 ml, weight 7.1 g, bed length 45 mm, input rate 0.263 ml/min) $\epsilon_{H_2O} = 22900$ cal/mole; K_0 mean = $3.7 \cdot 10^9$

Temp., °C	$m_{C_3H_6}$, ml/min · ml of catalyst	$lg K_0$	$\frac{\epsilon}{lg K_0} \cdot 10^{-3}$	$m_{C_3H_6}$, ml/min, calculated from ϵ_{H_2O} and K_0 mean
221	0,18	9,35	2,45	2,9
225	0,28	9,40	2,44	3,5
229	0,54	9,59	2,36	4,1
235	0,67	9,65	2,37	5,2
245	0,88	9,58	2,39	8,3
249	1,32	9,71	2,36	9,8
250	1,42	9,71	2,36	10,5
255	1,56	9,66	2,37	12,6
	Mean		2,39	

TABLE 5. Dehydrogenation of Cyclohexane on Partly and Completely Carbonized TiO₂
 Completely Carbonized TiO₂ (catalyst volume 10 ml, weight 7.1 g, bed length 45 mm, input rate 0.224 ml/min) $\epsilon = 25200$ cal/mole; K_0 mean = $4.9 \cdot 10^7$
 Partly Carbonized TiO₂ (catalyst volume 6.4 ml, weight 4.4 g, bed length 32 mm, input rate 0.224 ml/min) $\epsilon = 19000$ cal/mole; K_0 mean = $8.9 \cdot 10^5$

Temp. °C	m_{H_2} , ml/min · ml of catalyst	$lg K_0$	$\frac{\epsilon}{lg K_0} \cdot 10^{-3}$	Temp. °C	m_{H_2} , ml/min · ml of catalyst	$lg K_0$	$\frac{\epsilon}{lg K_0} \cdot 10^{-3}$
426	0,71	7,72	3,27	443	1,26	5,90	3,22
428	0,70	7,70	3,27	450	1,63	5,95	3,19
432	0,78	7,72	3,26	460	2,25	6,01	3,16
437	0,86	7,68	3,26	476	2,52	5,95	3,19
448	1,26	7,74	3,26	486	2,84	5,92	3,21
460	1,52	7,68	3,28				
470	1,74	7,64	3,30			Mean	3,19
479	2,27	7,66	3,28				
	Mean		3,27				

cases the reaction proceeded without side processes. The gaseous products contained up to 99% of hydrogen. The content of unsaturateds in the liquid catalyzate did not exceed 1% (490°), while unsaturateds were absent at 450°. The activity of the catalyst was constant in both cases. Table 5 gives data on the dehydrogenation of cyclohexane on both anatase surfaces. As this table shows, the difference in the activation energies and preexponential factors K_0 was considerable.

TABLE 6. Change in Cyclohexene Content of Catalyzate during Irreversible Catalytic Reaction on TiO_2

Temperature, °C	Catalyzate sample No.	Cyclohexene content, %
390	1	66.4
	2	75.0
	3	78.5
	4	82.0
437	1	50.5
	2	56.0
	3	60.0
449	1	58.4
	2	62.9
	3	68.5

TABLE 7. Dehydrogenation and Irreversible Catalytic Reaction of Cyclohexene on TiO_2 (catalyst volume 6.4 ml, weight 4.4 g, bed length 3.2 cm, input rate 0.263 ml/min)

Temp, °C	$\frac{m_{\text{H}_2}}{\text{ml/min ml of catalyst}}$	$\lg K_0$	$\frac{e}{\lg K_0} \cdot 10^{-3}$	Temp, °C	$\frac{m_{\text{H}_2}}{\text{ml/min ml of catalyst}}$	$\lg K_0$	$\frac{e}{\lg K_0} \cdot 10^{-3}$
403	1.09	8.40	3.08	300	0.078		
425	1.31	7.94	3.15	309	0.28	9.25	2.82
427	1.30	7.91	3.16	329	0.86	9.41	2.74
437	1.51	7.88	3.17	346	1.79	9.47	2.76
449	2.19	7.91	3.16	360	2.39	9.50	2.75
460	3.05	7.93	3.15	368	2.81	9.35	2.79
				381	4.70	9.41	2.78
				390	5.25	9.33	2.80
		Mean 7.95	3.15			Mean 9.44	2.80

Dehydrogenation and irreversible catalysis of cyclohexene. It was found that uncarbonized anatase promotes the irreversible catalytic reaction to a greater extent than carbonized anatase. This was confirmed by analysis of catalyzate samples taken at 10-min intervals during the experiments (Table 6). The irreversible catalytic reaction of cyclohexene was studied on uncarbonized TiO_2 over the range of 300-390° and dehydrogenation on carbonized TiO_2 over the range of 400-460°. The amount of cyclohexene reacting per min was found from the difference in the amounts of cyclohexene introduced and that which did not react. The percentage content of unreacted cyclohexene in the catalyzate collected in the first 7-8 min of the experiment was determined from the bromine numbers. Table 7 gives data on the dehydrogenation and irreversible catalytic reaction of cyclohexene. Both reactions were studied in the region where the equilibrium was displaced toward the forward reaction. Table 7 shows that while the activation energies were similar, K_0 of the irreversible catalytic reaction on uncarbonized TiO_2 was two orders higher than K_0 of dehydrogenation on carbonized TiO_2 .

Dehydrogenation of 1,4-cyclohexadiene. Like cyclohexene, 1,4-cyclohexadiene underwent dehydrogenation and an irreversible catalytic reaction on TiO_2 and, as in the case of cyclohexene, carbonization of the surface promoted dehydrogenation to a greater extent. Table 8 gives data for calculating the activation energy of 1,4-cyclohexadiene dehydrogenation.

TABLE 8. Dehydrogenation of 1,4-Cyclohexadiene on TiO_2 (catalyst volume 6.4 ml, weight 4.4 g, bed length 32 mm, input rate 0.263 ml/min) = 22300 cal/mole;
 K_0 mean = $2.4 \cdot 10^7$

Temp. °C	mH_2 , ml per min \times \times ml of catalyst	Log K_0	$\frac{\epsilon}{\lg K_0} \cdot 10^{-3}$
362	0,58	7,53	2,96
374	0,75	7,42	3,01
382	0,98	7,44	3,00
398	1,59	7,46	2,99
456	2,42	7,07	3,16
		Mean 7,38	3,02

It should be noted that in the case of cyclohexane dehydrogenation, the value of $\epsilon \cdot 10^{-3} / \lg K_0$, which characterizes the distribution of active centers, hardly changed with an increase in the carbonization of the TiO_2 surface (Table 5). The values of $\epsilon \cdot 10^{-3} / \lg K_0$ were constant during the dehydrogenation or dehydration of isopropanol on TiO_2 with various degrees of carbonization (Tables 2-4). In the dehydrogenation of cyclohexane, cyclohexene, or cyclohexadiene on completely carbonized TiO_2 , the value of $\epsilon \cdot 10^{-3} / \lg K_0$ also changed insignificantly (Tables 5, 7, and 8), which indicates that with a doublet mechanism for the dehydrogenation, the catalytic centers are not screened by extrinsic substituents.

SUMMARY

With the aid of a differential thermocouple it was possible to show that the gradual carbonization of the anatase surface occurring during an experiment completely suppressed the dehydrogenation of isopropanol and promoted its dehydration with the total activity of the catalyst remaining unchanged, suppressed the irreversible catalytic reaction of cyclohexene and cyclohexadiene, and promoted the dehydrogenation of cyclohexene, cyclohexadiene, and cyclohexane.

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KINETICS OF THE REACTION OF $n\text{-C}_3\text{H}_7\text{I} + \text{KI}^*$

IN NONAQUEOUS SOLVENTS AT PRESSURES UP TO 3000 kg/cm^2

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The kinetics of the isotopic exchange of $n\text{-C}_3\text{H}_7\text{I} + \text{KI}^*$ in ethanol and acetone were investigated in previous work [1, 2] and the electrical conductivity of solutions of KI in these solvents at pressures up to 2500 kg/cm^2 was measured. It was shown that this reaction proceeds by an ion-molecule mechanism in acetone and ethanol and that its rate in acetone at atmospheric pressure is approximately 200 times greater than in ethanol. With an increase in pressure, the rate of this reaction in ethanol increases and, on the contrary, the rate in acetone falls considerably. To explain the different effects of pressure on the rate of this reaction in ethanol and acetone, it was suggested that there is considerable desolvation of the I^- ion on formation of the activated complex.

To check this hypothesis, in the present work we investigated the effect of pressure on the rate of the reaction of $n\text{-C}_3\text{H}_7\text{I} + \text{KI}^*$ in methyl ethyl ketone and cyclohexanone and measured the electrical conductivity of solutions of KI in these solvents at various pressures

EXPERIMENTAL

The procedure for measuring the rate constants in the given solvents at various pressures was analogous to that described in [1]. The solvents and KI were prepared as in [2]. We should mention, however, that the sample of $n\text{-C}_3\text{H}_7\text{I}$ for preparing solutions of low concentrations (of the order of 0.001 M) was measured with an ultramicroburette [3]. The reaction rate constants were calculated from the formula derived for an ion-molecule mechanism [1] (with allowance for the change in the degree of dissociation of KI with an increase in pressure) and remained constant within the limits of experimental error with a change in concentration. The change in volume of the system on formation of the activated complex (ΔV^\ddagger) was calculated from formula (1).

$$\Delta V^\ddagger = -RT [(\partial \ln k_p / \partial p)_T + \kappa], \quad (1)$$

where the value of $(\partial \ln k_p / \partial p)_T$ was determined by graphical differentiation of the relation of $\log k_p$ to p , we obtained (k_p is the reaction rate constant at pressure p) and the value of κ , the isothermal compressibility of the solvent, was calculated from literature data [4].

The degree of dissociation of KI in methyl ethyl ketone and cyclohexanone was determined approximately, as in [2], from the ratio λ/λ_∞ , where λ is the equivalent electrical conductivity of the KI solution at the given concentration and pressure and λ_∞ is the corresponding value at infinite dilution. The measurement of the electrical conductivity of solutions of KI in the named solvents at various pressures and a given temperature and the treatment of the measurement results were the same as in [2]. The results of the electrical conductivity measurements are given in Table 1.

Analysis of the data in Table 1 shows that the equivalent electrical conductivity of the KI solutions and the ionization constant $K = \alpha^2 c / (1 - \alpha)$ in the two named solvents change quantitatively in the same way as in acetone and ethanol [2]. It should be noted, however, that the electrical conductivity of KI in cyclohexanone falls sharply (by a factor of approximately 10) with an increase in pressure from 800 to 1300 kg/cm^2 . The most probable reason for this considerable fall in electrical conductivity is a rapid increase in the viscosity of cyclohexanone with an increase in pressure over the given range. An approximate estimate of the increase in viscosity with an increase in pressure may be made with the aid of Walden's rule, according to which $\lambda_\infty \eta = \text{const}$ (η is the viscosity) for a given substance in various solvents. With the aid of Walden's rule we calculated the values of λ_∞ for solutions of KI in

TABLE 1. Electrical Conductivity of Methyl Ethyl Ketone and Cyclohexanone Solutions of KI

Cyclohexanone $t = 0^\circ$		Methylethyl ketone $t = 20^\circ$	
$c \cdot 10^3 \text{ M/l}$	$\text{cm}^2/\Lambda \Omega \text{M}$	$c \cdot 10^3 \text{ M/l}$	$\text{cm}^2/\Lambda \Omega \text{M}$
$p = 1 \text{ g/cm}^2$		$p = 1 \text{ kg/cm}^2$	
3,48	12,72	3,12	83,2
1,74	14,46	1,56	95,5
0,348	18,05	0,312	117
0,174	18,85	0,156	119
0	20,8(λ_∞)	0	131(λ_∞)
$p = 800 \text{ kg/cm}^2$		$p = 1000 \text{ kg/cm}^2$	
3,60	7,30	3,37	59,8
1,80	8,24	1,68	66,9
0,360	10,0	0,337	76,2
0,180	10,3	0,168	76,6
0	11,2(λ_∞)	0	83(λ_∞)
$p = 1300 \text{ kg/cm}^2$		$p = 2000 \text{ kg/cm}^2$	
3,65	1,08	3,53	44,1
1,83	1,25	1,77	47,5
0,365	1,38	0,353	51,8
0,183	1,48	0,177	50,7
0	1,57(λ_∞)	0	55(λ_∞)

acetone and ethanol at high pressures from the product $\lambda_\infty \eta$ at atmospheric pressure and literature data [5] on the viscosity of these solvents at various pressures and temperatures. Table 2 gives the results of these calculations. The experimental values of λ_∞ were taken from [2].

A comparison of the last two columns in Table 2 shows that there is good agreement between the experimental and calculated values of λ_∞ in acetone and ethanol. Thus, Walden's rule may be used apparently for approximate estimates of the values of λ_∞ for solutions of electrolytes at various pressures if the viscosities of the solvents at these pressures and the product $\lambda_\infty \eta$ at 1 atm are known and, conversely, it is possible to obtain the viscosities at various pressures with sufficient accuracy from known values of λ_∞ at these pressures. If the viscosity of cyclohexanone at 1 atm and 0° is taken as equal to 1, then if Walden's rule holds, the viscosity of this solvent at $p = 1300 \text{ kg per cm}^2$ and the same temperature will equal ~ 12 . This considerable increase in the viscosity of cyclohexanone is probably connected with the fact that cyclohexanone solutions of KI at a pressure of $\sim 1800 \text{ kg/cm}^2$ freeze at 0° and consequently, cyclohexanone solutions at 1300 kg/cm^2 are close to the freezing point

TABLE 2. Values of λ_∞ Obtained Experimentally and Calculated by Walden's Rule ($t = 20^\circ$)

Solvent	$P, \text{ kg/cm}^2$	$\eta \cdot 10^3, \text{ poise}$	$\lambda_\infty \eta$	$\lambda_\infty \text{ calc.}$	$\lambda_\infty \text{ exp.}$
Ethanol	1	12	0,571	(47,5)	47,5
	1500	21		27,2	28,5
	2500	30		19	21,5
Acetone	1	3,3	0,589	(178,5)	178,5
	1500	6,7		88	90,2
	2500	9,2		64	63,5

The results of studying the kinetics of the reaction of $n\text{-C}_3\text{H}_7\text{I} + \text{KI}^*$ in methyl ethyl ketone and cyclohexanone at various pressures are given in Table 3.

The data in Table 3 show that the reaction we studied is slowed by an increase in pressure and the use of methyl ethyl ketone as the solvent; at the same time, the rate constant of this reaction in cyclohexanone increases with an increase in pressure.

DISCUSSION OF EXPERIMENTAL RESULTS

According to formula (2)

$$\Delta V^\ddagger = \Delta V_0^\ddagger + \Delta V_s^\ddagger - \Delta V_{is}, \quad (2)$$

which was proposed in [6], the reaction of $n\text{-C}_3\text{H}_7\text{I} + \text{I}^-$ in a solvent may be represented as the following cycle: 1) the transfer of a $n\text{-C}_3\text{H}_7\text{I}$ molecule and I^- ion from an infinitely dilute solution to vacuum at an infinite distance from each other (volume change $-\Delta V_{is}$); 2) the formation of an activated complex in vacuum (volume change ΔV_0^\ddagger); 3) the transfer of the activated complex into the solvent (volume change ΔV_s^\ddagger); 4) decomposition of the activated complex and separation of the reacting particles in the solvent to infinity (volume change ΔV^\ddagger).

The value of ΔV_{is} approximately equals the sum of the volume effects of solution of I^- and $n\text{-C}_3\text{H}_7\text{I}$, extrapolated to infinite dilution. The magnitude of the error of this approximation is determined by the difference in the volumes of the particles in the pure substance and in vacuum. Since the volume effect of solution of I^- is

TABLE 3. Rate Constants of the Reaction of $n\text{-C}_3\text{H}_7\text{I} + \text{KI}$ *

Solvent	P, kg/cm ²	Temp., °C	c · 10 ³ , mole/liter		k · 10 ³ , mole/liter sec
			n-C ₃ H ₇ I.	KI	
Methyl ethyl ketone	1	20	2-7	2-7	75
	2000	20	2	2	54
	3200	20	2	2	46
Cyclohexanone	1	0	3-5	1-3	23
	800	0	2-3	2-3	29
	1300	0	2	2	33
	1400	0	2	2	38
	1500	0	2	2	36

incomparably greater than for $n\text{-C}_3\text{H}_7\text{I}$, we used the approximation $\Delta V_{is} = \frac{\Delta V_{\infty}}{2}$, where ΔV_{∞} is the volume effect of solution of KI at infinite dilution. We measured the volume effects of solution of KI in methyl ethyl ketone and cyclohexanone at various concentrations. The values of $\Delta V_{\infty}/2$ found from the results of these measurements were -33 and about -20 cc/mole, respectively, i.e., the volume effect of solvation of the I^- ion in methyl ethyl ketone solution is considerably greater than in cyclohexanone solution. At the same time, the values of ΔV^\ddagger calculated from the data in Table 3 by means of equation (1) were +2 cc/mole in methyl ethyl ketone and -9 cc/mole in cyclohexanone, i.e., they differed even in sign. Analogous relations of the values of $\Delta V_{\infty}/2$ and ΔV^\ddagger were found in the previous investigation of the same reaction in acetone and ethanol [1]. The negative value of the volume effect of solution of KI in acetone was considerably greater than in ethanol; the value of ΔV^\ddagger in acetone was positive, while that in alcohol was negative.

Let us now examine the other values in equation (2). The estimated value of $-\Delta V_0^\ddagger = 10\text{-}14$ ml/mole [2]. As regards ΔV^\ddagger , we consider that it is less in absolute value than ΔV_{is} , i.e., we assume that the I^- ion in the activated complex reacts with the solvent more weakly than outside the complex, so that the contraction of the solvent becomes less. The reason for this weakening of the interaction could be, for example, dispersal of the electron shell of the I^- ion on formation of a bond with the $n\text{-C}_3\text{H}_7\text{I}$ molecule. The data presented above show that with low negative values of $\Delta V_{\infty}/2$, the reaction of $n\text{-C}_3\text{H}_7\text{I} + \text{I}^-$ accelerates with an increase in pressure and with high negative values of $\Delta V_{\infty}/2$, it decelerates. This is compatible with the hypothesis that the I^- ion is partly desolvated during the formation of the activated complex as the increase in volume of the system during this desolvation of the ion may be greater in absolute value than the contraction of the system due to the formation of the activated complex.

In conclusion, we would like to thank laboratory assistant V. V. Bogacheva for daily help with the work.

SUMMARY

1. The rate constants of the reaction of $n\text{-C}_3\text{H}_7\text{I} + \text{KI}$ at pressures up to 3000 kg/cm² in methyl ethyl ketone at 20° and cyclohexanone at 0° were measured.
2. We measured the electrical conductivities of solutions of KI in these solvents at various pressures and the volume effects of solution of KI at atmospheric pressure.
3. The results of the investigation are compatible with the hypothesis that the iodine ion is partly desolvated during the formation of the activated complex in the ion-molecular isotopic exchange studied.

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ADSORPTION STUDY OF ALUMINUM OXIDE MONOHYDRATE AND γ -ALUMINUM OXIDE

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Comparison of the adsorption of various gases and vapors on catalysts and adsorbents of the same chemical nature makes it possible to draw a number of conclusions on the relative adsorption energy, the orientation of the adsorbed molecules, the possibility of two-dimensional phase transitions, the role of interaction in the adsorbed layer, and the heterogeneity of the surface. There are now a vast number of papers on the adsorption of various substances, but the above comparison is impossible in most cases as in the work of different authors, the catalyst samples of the same chemical nature differed to a considerable extent in the preparation methods, thermal treatment conditions, porous structure, and content of impurities and surface-active groups.

We undertook a comprehensive study of the adsorption properties of aluminum oxide monohydrate (boehmite) and its dehydration products with respect to Ar, N₂, n-C₆H₁₄, C₆H₆, and CH₃OH. In this communication we present the results of studying the adsorption of argon, nitrogen at -195°, and n-hexane and benzene at 20° on the same samples.

EXPERIMENTAL

As the starting preparation we used aluminum hydroxide, which was prepared by precipitation from 10% Al(NO₃)₃ solution with 10% NH₄OH solution and then treated as described in [1], where the most important data on all the samples obtained from it (including the results of phase analysis) are given.

The adsorption study was carried out in an original, jointless vacuum apparatus, which consisted of three main sections: 1) a volumetric apparatus, 2) an apparatus with a vacuum microburette, and 3) a gas purification system. All the sections were mounted on one welded stand and served by one vacuum point. The low pressure produced by VN-461 and TsVL-100 pumps was measured with a VIT-1 vacuum gauge, operating with LT-2 and LM-2 heads, in the subsidiary part of the apparatus and with McLeod gauges in the working part. The apparatus (Fig. 1) made it possible, firstly, to study both the adsorption of gases volumetrically and the adsorption of vapors with the vacuum microburette on the same catalyst sample, and, secondly, to make measurements simultaneously on two samples. The volumetric part of the apparatus consisted of a bulb gas burette, a McLeod gauge, a U-shaped manometer, and ampoules with the catalyst. The working part of the apparatus was connected to bulbs containing the main stock of gases. The volume of the bulb burette (179.75 cc) was measured beforehand with mercury with an accuracy of about 0.03%. The dead volume of the gas distribution system was measured with helium and found to be 24.25 cc \pm 0.8% (without the bulb burette).

The apparatus with the vacuum microburette was similar to that described in [2]. Both apparatuses were enclosed in an air thermostat, the temperature of which was kept at 25° with an accuracy of about 0.2°. The temperature-sensitive element was an inertialess copper resistance thermometer ($R = 53.00$ ohm), connected in the arm of an EMV-21 electronic automatic control bridge. The temperature of the microburette and ampoules with the catalyst was maintained with an accuracy of $\pm 0.02^\circ$ by means of ultrathermostats. The positions of the mercury menisci in the U-manometer and those of the organic liquids in the microburette were determined with an accuracy of about 0.01 mm with a KM-6 cathetometer. The accuracy of the determination of the amount of adsorption by means of the liquid microburette with a 1-g sample and n-C₆H₁₄ was $\sim 3 \gamma$ or 0.3μ mole/g of catalyst. The accuracy of the determination of the amount of adsorption by the volumetric method theoretically exceeded 3γ with the same sample, but the introduction of corrections for thermal diffusion and for the "cold" part of the "dead" space reduced this accuracy in practice. The liquid nitrogen temperature was measured with a gas thermometer. A graph of the

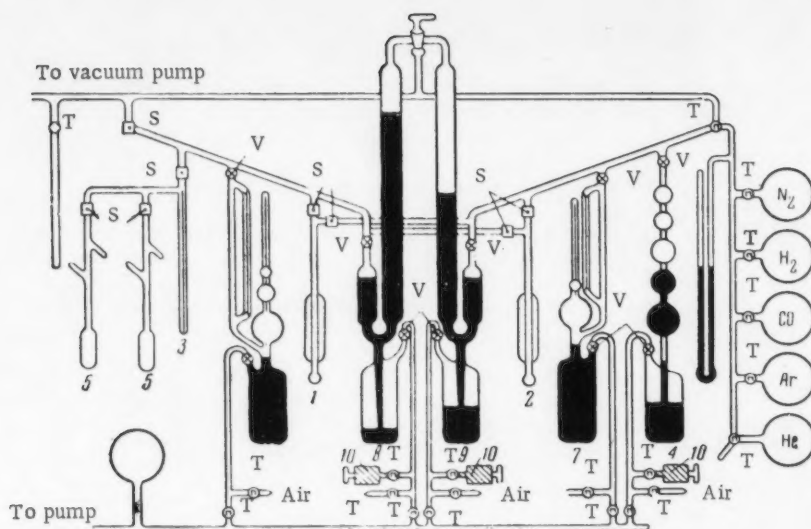


Fig. 1. Plan of adsorption apparatus: ampoules with catalyst (1, 2), liquid micro-burette (3), gas burette (4), liquid storage vessels (5), McLeod gauges (6, 7), U-manometers (8, 9), syphon bellows (10), seals (S), valves (V), and taps (T).

temperature dependence of the saturated vapor pressure of nitrogen and argon was constructed from the equations of Born [3] and Dodge [4].

The sequence of adsorbates used in the adsorption experiments was as follows: nitrogen, argon, $n\text{-C}_6\text{H}_{14}$, C_6H_6 , and nitrogen (repeat). Each adsorption isotherm was obtained from several series of experiments. Before each series and before the use of the next adsorbate, the Al_2O_3 samples were pumped out to high vacuum at appropriate temperatures.

The starting nitrogen and argon contained traces of moisture, oxygen, and other gases. Therefore, before the bulbs were filled, the gases were passed through the purification system, which consisted of a column filled with an oxygen absorber, namely, silica gel impregnated with copper [5], bottles with sodalime for the absorption of carbon dioxide, columns with drying agents (silica gel, alumina, and phosphorus pentoxide), and traps cooled with liquid nitrogen. The nitrogen present in the argon was absorbed at 600° in a steel U-tube filled with calcium activated with magnesium [6].

The hydrocarbons were first freed from moisture, air, and impurities. The benzene and n -hexane were purified by distillation over sodium; they were then outgassed in the vacuum apparatus by repeated pumping out of the frozen liquid and thawing of the latter without pumping.

EXPERIMENTAL RESULTS AND DISCUSSION

Nitrogen and argon. Experimental isotherms for the adsorption of nitrogen vapor at -195° are given in Fig 2.a. These isotherms were obtained over the range of relative pressures from 0 to $p/p_s = 0.3$. The relative positions of the isotherms give a qualitative idea of the surface of the samples as the amount of adsorption in this part of the isotherm is proportional to the specific surface. The same is true of the adsorption isotherms for argon at -195° , which are given in Fig. 2, b. Each sample of alumina gel was used for several adsorption determination cycles with evacuation of the samples between cycles at the same temperature and pressure as in the initial treatment. This procedure gave satisfactorily consistent results and complete reproducibility of the isotherms. This showed that the successive changes in the adsorption of different substances on the same sample with intermediate evacuation did not distort the results appreciably.

Since the adsorption measurements were made by the volumetric method and the subsequent loss in weight of the samples during heating and evacuation was not determined with sufficient accuracy, the amounts of adsorption for all the adsorbed substances were related to 1 g of starting samples 1 and 2, which were evacuated at a separate vacuum point.

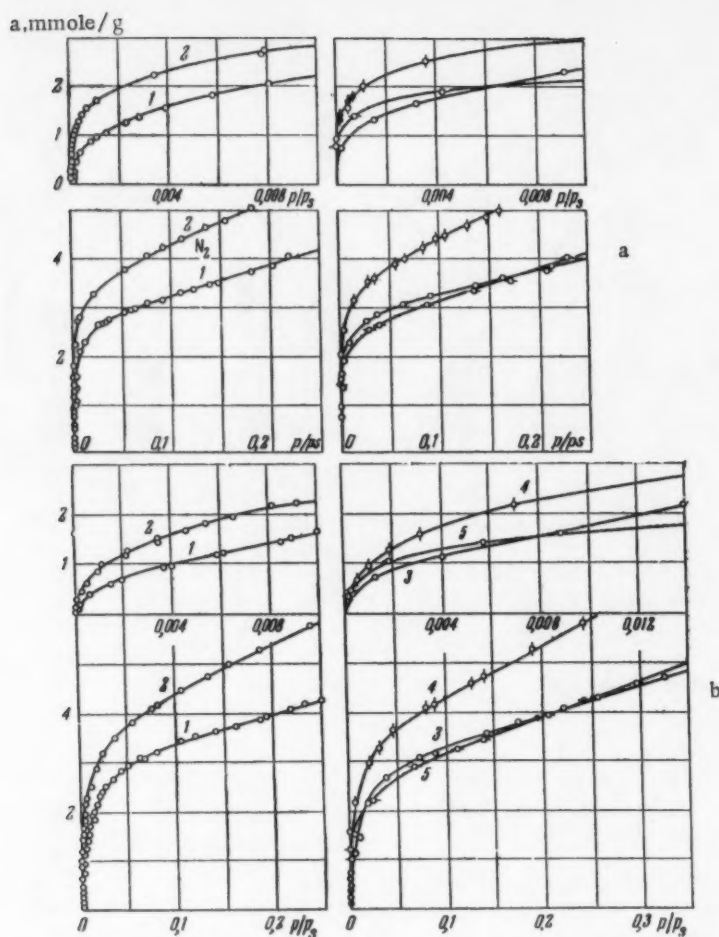


Fig. 2. Adsorption isotherms for nitrogen (a) and argon (b) at -195° on samples 1-5.

For determining the specific surface of the samples tested we decided to use only two calculation methods, namely, the simplest, point B method (denoted by $S_{p.B.}$) and the standard BET method (S_{BET}). As was shown in [7, 8], the Harkins-Jura and Huttig methods lead to a greater discrepancy in the surface areas than the methods we chose. Both the point B method and the BET method are graphical, but the former is more approximate.

Figure 3 gives the experimental adsorption isotherms. they are described satisfactorily by the BET equation. The specific surface was calculated by the usual formula:

$$S = a_m \cdot N_A \cdot \omega_0, \quad (1)$$

where a_m is the capacity of a monolayer of the given adsorbate in mmole/g, N_A is Avogadro's number ($6.02 \cdot 10^{23}$ molecules), and ω_0 is the area of one molecule of the adsorbate in a close-packed monolayer. Many authors have adopted the value $\omega_0 = 16.2 \text{ \AA}^2$ at $T = 78^{\circ}\text{K}$ for nitrogen, while data on ω_0 for argon are contradictory. Emmett and Brunauer [9] considered it as equal to 14.4 \AA^2 , in the work of Emmett and Cines [10] it was assumed that $\omega_0 = 15.4 \text{ \AA}^2$, and Corrin [11], who studied adsorption on carbon blacks, adopted the value 16.6 \AA^2 . Rhodin [12] considered that it equals 15.2 \AA^2 . Krapova [13] estimated it from literature data on the adsorption of argon on carbon blacks and obtained the value $\omega_0 = 14.7 \text{ \AA}^2$. In our calculations of the specific surface, like Emmett and Cines [10], we adopted the value $\omega_0 = 15.4 \text{ \AA}^2$ for argon. Table 1 gives the values of a_m , the constants of the BET equation, C , S_{BET} , and $S_{p.B.}$. Table 1 shows that in practice, both adsorbates give good agreement of the values of S calculated according to the BET equation. The point B method gives values of S that differ by not more than 10%, i.e., both methods—the

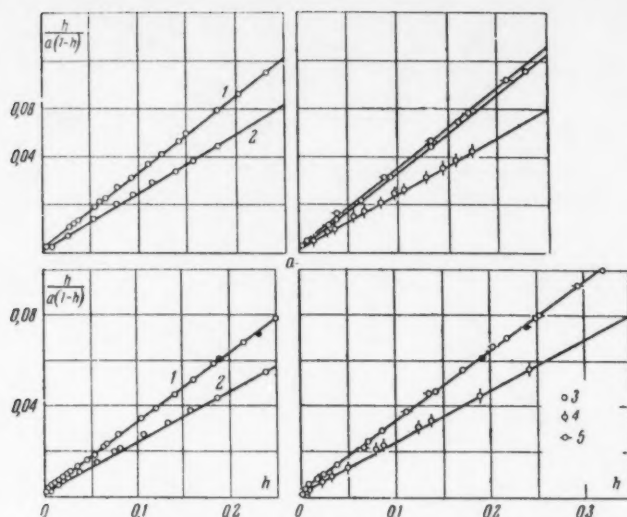


Fig. 3. Adsorption isotherms for nitrogen (a) and argon (b) at -195° on samples 1-5 in the coordinates of the BET equation (black points represent desorption).

TABLE 1. Specific Surface of Alumina Gel Samples

Al ₂ O ₃ sample	Argon				Nitrogen			
	$a_{m'}$ mmole/g	c	S_{BET} m ² /g	$S_{P.B.}$ m ² /g	$a_{m'}$ mmole/g	c	S_{BET} m ² /g	$S_{P.B.}$ m ² /g
1	3,34	83	311	300	3,20	104	312	302
2	4,60	60	427	400	4,20	80	425	405
3	3,29	84	306	286	3,11	160	303	300
4	4,68	45	436	400	4,48	80	437	426
5	3,32	83	308	280	3,13	90	305	290

point B method and the BET method—are in satisfactory agreement, but in the case of nitrogen, the values of S obtained by the two methods are much closer. Thus, using the molecular areas of 16.2 and 15.4 Å² for nitrogen and argon, in practice we obtained unequivocal numerical results for the specific surfaces of all five samples.

Thus, like the results we gave in [1], our measurements showed that argon ($\omega_b = 15.4$ Å²) and nitrogen ($\omega_b = 16.2$ Å²) as adsorbates give adequate values for the surface.

n-Hexane. Figure 4 gives adsorption isotherms for n-C₆H₁₄ vapor on the samples studied. The upper part of Fig. 4 gives the initial sections of the isotherms. The amounts of adsorption per g of starting sample (1 and 2) are given. Figure 4 shows that the isotherms for samples 1, 3, and 5 and 2 and 4, respectively, coincide in the initial region. A small difference was observed in the region of high relative pressures. These isotherms indicate that the transitions A-1 → A-3 → A-5 → A-4, which occurred in high vacuum at a high temperature, involve hardly any change in the surface and pore volume. The change in the pore diameter under these conditions was small. Differential pore-diameter distribution curves are given in Fig. 5. Figure 5 clearly shows that samples A-1, A-2, and A-3 have a fine pore distribution with equal effective predominating pore diameters, which equal 38 Å without a correction for the thickness of the adsorbed film; with allowance for the correction, $d = 48$ Å. The pore distribution curve was determined by applying the Kelvin equation to the desorption branch of the isotherms.

A small increase in the pore diameter occurred when the temperature was raised to 360° ($d = 50$ Å with correction for the thickness of the layer) and a more appreciable increase with a rise in temperature to 420° ($d = 58$ Å). However, the distributions were similar with a sharp peak for all the samples.

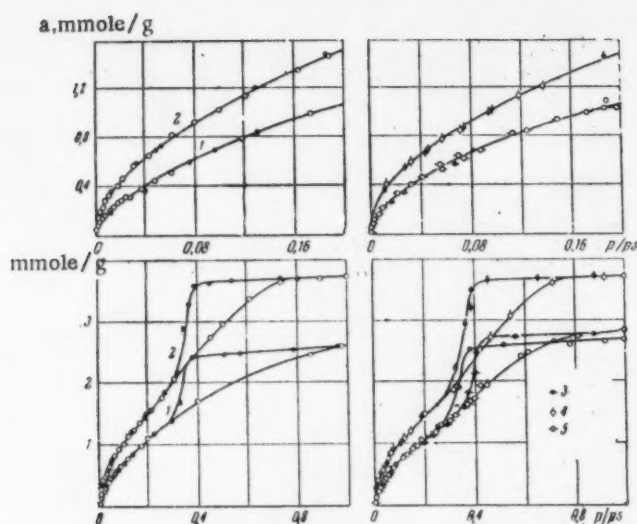


Fig. 4. Adsorption isotherms for $n\text{-C}_6\text{H}_{14}$ vapor on samples 1-5 at 20°

TABLE 2. Structural Characteristics of Sample from $n\text{-C}_6\text{H}_{14}$ Adsorption Data and Constants of the BET Equation

Al_2O_3 sample	a_m , mmole/g	C	ω , Å ²	d, Å without correction	S' , m ² /g	V_s' , cc/g	$d = \frac{4V}{S}$
1	1,26	10	41	37	160	0,34	44
2	1,67	11	42	38	262	0,48	45
3	1,23	11	41	38	173	0,35	46
4	1,49	15	48	40	234	0,48	44
5	1,04	14	47	44	168	0,36	48

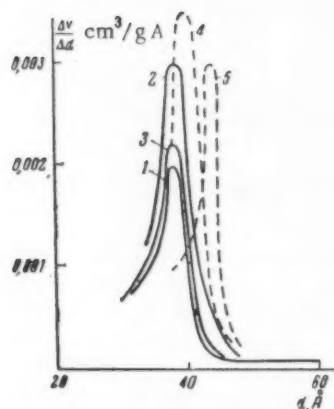


Fig. 5. Pore volume-size distribution curves for samples 1-5.

We found that the BET equation held formally over the range of p/p_s from 0.05 to 0.35 for all five samples (with the exception of the desorption points in the hysteresis region) and it was used for determining the constants a_m and C.

Table 2 gives the values of a_m , C, and ω_0 ; the latter was determined from the equation:

$$\omega_0 = \frac{s}{a_m N_A} \quad (2)$$

where s is the surface of the sample calculated from the adsorption of argon vapor and N_A is Avogadro's number. The value of a_m was determined graphically.

Table 2 also gives the values of S' , i.e., the surface of the multimolecular film formed by the beginning of capillary condensation [14]. These values were calculated from the thermodynamic equation of capillary condensation:

$$S = - \int_{a_1}^{a_s} \frac{A \cdot da}{a} \quad (3)$$

where A is the work of the vapor in contraction of the film surface and a_1 and a_s are the amounts of adsorption corresponding to the beginning and end of capillary condensation. Table 2 shows that the values of S' are approximately

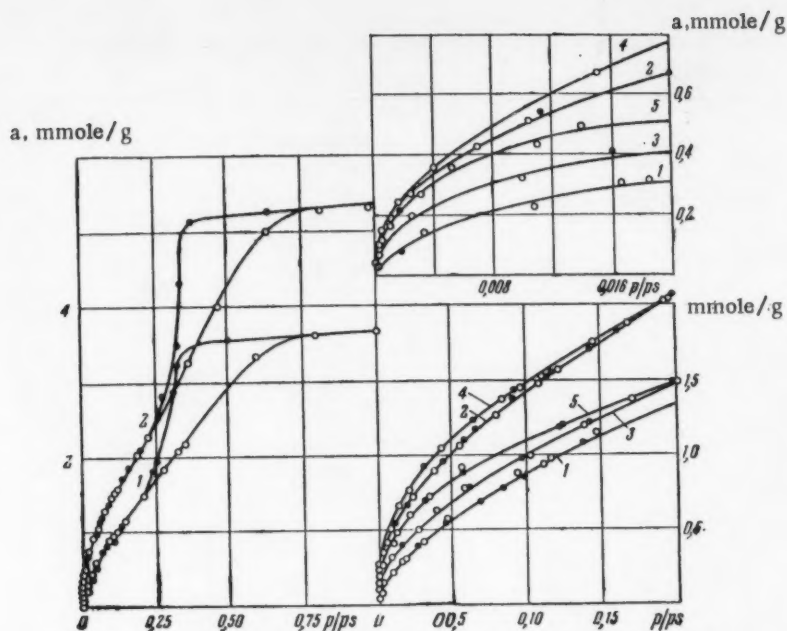


Fig. 6. Adsorption isotherms for C_6H_6 vapor on samples 1-5 at 20° .

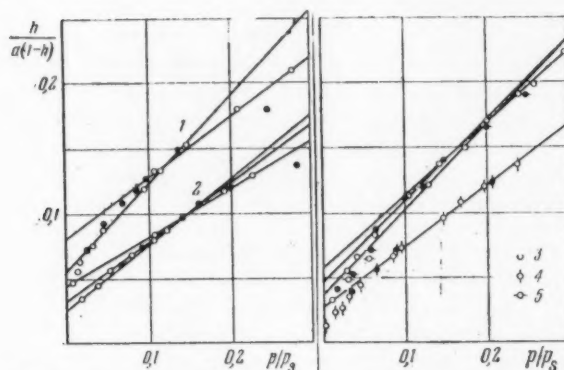


Fig. 7. Check of the applicability of the BET equation to the adsorption of C_6H_6 .

one half those of S, which shows that the sample investigated are sorbents of mesium porosity [14]. It is therefore probable that the calculated values of ω_b for C_6H_{14} are less than the expected ones, especially for samples 1, 2, and 3, which have narrower pores.

The following values of ω_b for C_6H_{14} molecules are given in the literature: 60.6 \AA^2 for adsorption on $(NH_4)_3PO_4 \cdot 12 MoO_3$ [15], 64.0 \AA^2 on anatase [16], 51.5 \AA^2 on carbon black [17], and 72 \AA^2 on quartz [18]. Our values are all less than these and this may be explained by high adsorption of $n-C_6H_{14}$ due to the presence of a large number of medium pores.

Table 2 gives the values of the total pore volume V_s , calculated from the horizontal section of the hysteresis at $p/p_s = 1$ and the average pore diameters \bar{d} , calculated from the simplified expression for the cylindrical model of a pore. The latter values are close to those obtained from Kelvin's equation with a correction for the thickness of the adsorbed layer.

TABLE 3. Constants of the BET Equation for C_6H_6 Adsorption and Data on the Structure of the Samples

Al_2O_3 sample	V_s , cc/g	S , m^2/g	$d = \frac{4V_s}{S}$	a_m , mmole/g	ω_b , \AA^2	C_{BET}	d_k \AA
1	0,33	250	42	1,83—1,55	29—41	8—15	37
2	0,48	270	45	2,08—2,89	29—41	9—14	38
3	—	—	—	1,67—1,50	30—34	10—14	—
4	—	—	—	2,06	35	16	—
5	—	—	—	1,44	35	19	—

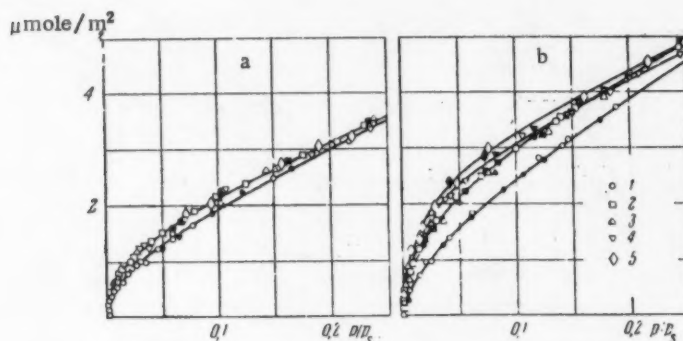


Fig. 8. Absolute adsorption isotherms for $n-C_6H_{14}$ (a) and C_6H_6 (b) on samples 1-5.

Benzene. Experimental isotherms for the adsorption of benzene vapor are given in Fig. 6. The left-hand part of this figure gives only two isotherms for samples 1 and 2 over the whole range of relative pressures. The right-hand part gives the initial sections of the adsorption and desorption isotherms for the five samples studied. The full isotherms show wide hysteresis with a sharply falling desorption branch. In the initial region (see right top) there is a fan of isotherms that distinguishes the adsorption of benzene from the adsorption of n -hexane, for which the order of the isotherms apparently depends solely on the specific surface.

It seemed interesting to estimate the surface of our samples from the adsorption of benzene. As Fig. 7 shows, for samples obtained at temperatures from 20 to 300° and containing a large amount of water, the BET equation does not hold well in practice over the pressure range from 0.05 to 0.30; samples A-4 and A-5 are exceptions and for them, the points of the isotherm fall on a straight line well over the pressure range from 0.05 to 0.25. The deviation from the BET equation for the adsorption of C_6H_6 with our samples apparently is explained by the different degrees of wetness of our samples, which has a stronger effect on the adsorption of C_6H_6 than that of $n-C_6H_{14}$ (see below).

Figure 7 gives the possible straight lines, between which the experimental points lie. It is possible to estimate the limiting values of a_m , assuming that the BET equation holds for the adsorption of benzene. Table 3 gives the values of V_s , S , d , ω_b , and C_{BET} in addition to a_m . Tables 2 and 3 show that the total pore volumes and the predominant pore diameters for samples 1 and 2 calculated from data on the adsorption of benzene and hexane are the same and consequently the pores are equally accessible to these adsorbates.

As in the case of $n-C_6H_{14}$, the values of ω_b for C_6H_6 were less than the expected ones and apparently this was also caused by the characteristics of the texture and chemical nature of the catalyst. In calculating the specific surface of solids it is usually assumed that $\omega_b = 39-48 \text{ \AA}^2$ for the C_6H_6 molecule, depending on the chemical nature of the surface. Therefore if we attempt to estimate the surface of our samples from benzene adsorption, assuming that $\omega_b = 42 \text{ \AA}^2$ (we used this value in our work for calculating the surface of catalysts based on alumina [19, 20]), we obtain a value for the surface which exceeds the value calculated from the adsorption of nitrogen and argon. Thus, our results indicate that the specific surfaces of samples obtained under the conditions described above calculated by the BET method from the adsorption of C_6H_6 or $n-C_6H_{14}$ are of an arbitrary nature to some extent and lead to anomalously high values of S if the given values are adopted for the molecular areas of C_6H_6 and $n-C_6H_{14}$. This anomaly is

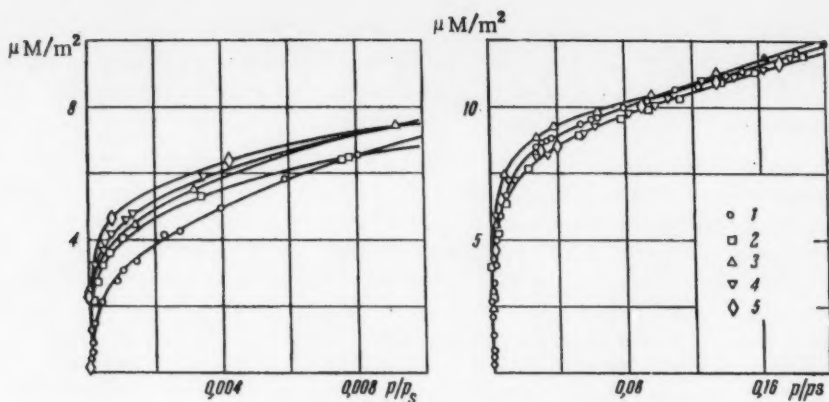


Fig. 9. Absolute isotherms for the adsorption of nitrogen vapor.

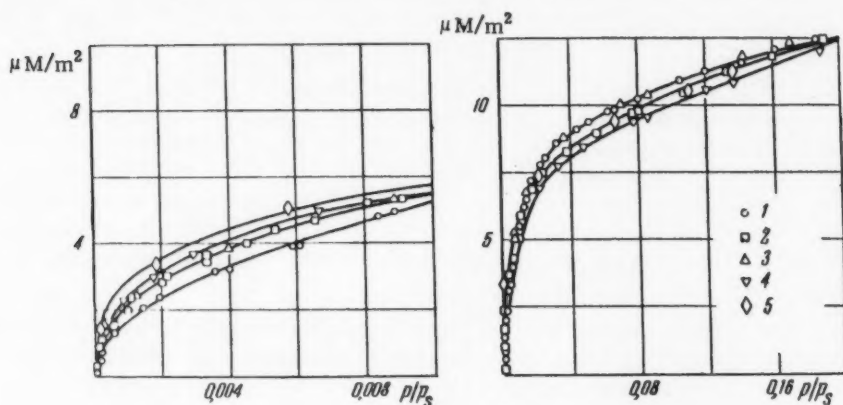


Fig. 10. Absolute isotherms for the adsorption of argon.

caused by the high energy of sorption in the developed texture of the system $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$ and its dependence on the H_2O content.

Effect of dehydration of Al_2O_3 on the adsorption of $n\text{-C}_6\text{H}_{14}$ and C_6H_6 . In order to elucidate the effect of a change in the chemical nature of the surface on the adsorption of any gas (or vapor), it is expedient to construct "absolute" (relative to unit surface) isotherms. Figure 8 compares absolute isotherms for the adsorption of $n\text{-C}_6\text{H}_{14}$ and C_6H_6 . These isotherms were obtained from the experimental isotherms by dividing the amount of adsorption (expressed in mmole/g) by the specific surface calculated from the adsorption of argon vapor.

Figure 8 shows that in the case of $n\text{-C}_6\text{H}_{14}$, the absolute adsorption isotherms for Al_2O_3 samples 2, 3, 4, and 5 coincide and consequently, dehydration over the temperature range of $120\text{-}420^\circ$ or, in other words, the H_2O content of the Al_2O_3 does not affect the adsorption of $n\text{-C}_6\text{H}_{14}$, while the absolute adsorption isotherm for $n\text{-C}_6\text{H}_{14}$ on boehmite (sample A-1) lies below. Since the porous structure of the samples we studied remained practically unchanged during the thermal treatment, the lower adsorption of $n\text{-C}_6\text{H}_{14}$ on sample A-1 (boehmite) in comparison with the adsorption on the other samples ($\gamma\text{-Al}_2\text{O}_3$) was evidently caused by the difference in the nature of these substances and the structure of their crystal lattices. It is evident that the more compact structure of $\gamma\text{-Al}_2\text{O}_3$ is responsible for the high dispersion energy of the adsorption forces. Generally speaking, this should also apply to the adsorption of C_6H_6 (see right-hand part of Fig. 8). However, the increased sensitivity of the adsorption of C_6H_6 to the H_2O content of the Al_2O_3 makes a substantial contribution to the total adsorption interaction so that progressive dehydration of $\gamma\text{-Al}_2\text{O}_3$ (the H_2O content of the $\gamma\text{-Al}_2\text{O}_3$ was reduced to 4%) increased the adsorption of C_6H_6 .

The increase in the adsorption of C_6H_6 may be connected with the appearance of narrow pores with a high adsorption potential, but this effect was found to be almost identical for C_6H_6 and $n\text{-C}_6\text{H}_{14}$ adsorption due to the similar

ionization potentials (9.8 and 10.43 eV), mean polarizability ($10.32 \cdot 10^{-24}$ and $11.78 \cdot 10^{-24} \text{ cm}^3$), and mean diamagnetic susceptibility ($123.0 \cdot 10^{-30}$ and $32.0 \cdot 10^{-30} \text{ cm}^3$) of these molecules. An increase in the adsorption potential due to the ordering of the surface layers of $\gamma\text{-Al}_2\text{O}_3$ should therefore lead to the same type of change in the sequence of the isotherms.

It seems to us that there remains one sound possibility for explaining the phenomenon found on the basis of a donor-acceptor interaction of the π -electrons of the aromatic ring with the hydrated, negatively charged surface of the $\gamma\text{-Al}_2\text{O}_3$. In this connection, it is interesting to compare the absolute isotherms for the adsorption of argon and nitrogen on the same samples. Figures 9 and 10 give these isotherms. The left-hand part gives the initial sections of the isotherms. Figures 9 and 10 show that the adsorption of argon and nitrogen on boehmite is also less than on $\gamma\text{-Al}_2\text{O}_3$. Nonetheless, the absolute isotherms for both nitrogen and argon do not coincide for $\gamma\text{-Al}_2\text{O}_3$. In the case of nitrogen, the effect of dehydration of SiO_2 on its adsorption was elucidated in [13]; it was found that the removal of surface OH groups, which occurs at 300-900°, is accompanied by a fall in the adsorption of nitrogen in the same way as in the case of benzene. In the case of $\gamma\text{-Al}_2\text{O}_3$, there is an increase in nitrogen adsorption with dehydration over the temperature range studied and this may also be explained either by the formation of surface polarizing complexes due to adsorption, by the creation of microroughness by dehydration of the surface, or by the removal of water blocking the adsorption center of Al_2O_3 . The adsorption potential is high in the microcracks formed and the nitrogen and argon isotherms lie above the isotherms of the starting samples.

Thus, the degree of dehydration of $\gamma\text{-Al}_2\text{O}_3$ over the range from 11.6 to 4.0 weight % of H_2O does not affect the adsorption of $n\text{-C}_6\text{H}_{14}$, but appreciably increases the adsorption of C_6H_6 , nitrogen, and even argon in the initial monomolecular region (up to $\theta = 0.4$ for N_2 and Ar). The higher adsorption of nitrogen in comparison with the adsorption of argon in the initial region is explained by the higher adsorption energy of nitrogen in comparison with that of argon due to the additional energy of the interaction of the nitrogen quadrupole with the electric field of $\gamma\text{-Al}_2\text{O}_3$. The quadrupole moment of argon equals zero. Qualitative conclusions on the adsorption energies of nitrogen and argon may also be drawn from the constant C of the BET equation given in Table 1. This constant for argon is usually less than the corresponding value for nitrogen.

The adsorption of the vapors studied on aluminum hydroxide (boehmite) is low due to the fact that boehmite has a more open lattice containing hydroxyl groups "perturbed" by their close proximity to each other, than $\gamma\text{-Al}_2\text{O}_3$ with more close-packed oxygen and aluminum atoms, which are partly or completely ionized.

SUMMARY

1. The thermal conversion of boehmite to γ -alumina was studied by an adsorption method. Detailed structural characteristics of five samples with different H_2O contents were determined.
2. The absolute isotherms for the adsorption of argon and nitrogen at -195° and $n\text{-C}_6\text{H}_{14}$ and C_6H_6 at 20° were calculated. It was established that boehmite adsorbs less than $\gamma\text{-Al}_2\text{O}_3$.
3. A change in the concentration of hydroxyl groups in alumina was found to affect the adsorption of benzene, but not the adsorption of n -hexane.

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MECHANISM OF INTRAMOLECULAR OXIDATION-REDUCTION REACTIONS OF α -HYDROXY AND α -HALO CARBONYL COMPOUNDS

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For a very long time there have been constant discussions in the literature of the mechanisms of the reactions of organic compounds [1]. In the last thirty years science has been enriched by new methods for the study of reaction mechanism, and general mechanisms have been proposed for groups of reactions on the basis of electronic concepts. Earlier, particularly at the end of the last century, it was usual to regard the mechanisms of the reactions of organic compounds in terms of hypotheses concerning the parts played by intermediate substances of low stability which were isomeric to the reactants or products. Frequent recourse was had also to the hypothesis of unstable molecular compounds (complexes) between the starting substances and the reagent. In appraising the still incomplete information on reaction mechanisms and the unabating interest in this problem, we may remember the statements concerning the evolution of science made by that great leader of the workers and scientists of genius V. I. Lenin, to whom this Session of the Academy of Sciences of the USSR is dedicated on the occasion of the ninetieth anniversary of the date of his birth. In his foundation-laying work "Materialism and Empiriocriticism," which was written in 1909, Vladimir Il'ich wrote: "It is necessary to discuss in a dialectical fashion. . . to analyze in what way knowledge comes into being out of lack of knowledge, in what way incomplete inaccurate knowledge becomes more complete and more accurate." * Though the question of the mechanisms of the reactions of organic compounds is at the lower stages of its evolution, being a very complex matter, we may be sure that in the future reliable ways will be found for the more complete elucidation of reaction mechanisms on the basis of new developments in chemistry and physics.

The mechanisms of reactions of simultaneous oxidation and reduction are of particular interest. These reactions are extremely varied, and they are characteristic of many organic substances, particularly in important biological processes. Reactions of simultaneous oxidation and reduction must be acknowledged as examples of the strongly marked chemical affinity of atoms of carbon, hydrogen, and other elements to oxygen atoms. The separation of these reactions into a special group has found considerable support in the electronic treatment of oxidation-reduction phenomena. In the papers by Danilov [2] two types of reaction of simultaneous oxidation and reduction are distinguished: intramolecular oxidation-reduction reactions and intermolecular oxidation-reduction reactions. In an intramolecular oxidation-reduction reaction there is a redistribution or concentration of atoms of oxygen and hydrogen (and radicals) in different parts of one and the same molecule. Intermolecular oxidation-reduction reactions proceed with change in composition due to addition of alkali, as in the benzil rearrangement and Cannizzaro reaction, or to addition and elimination of water.

Favorskii examined and discovered many reactions, including many important reactions of simultaneous oxidation and reduction (isomerization of keto alcohols, etc.), and these form a very valuable contribution to chemistry [3, 4]. We must make particular note of the great significance of Favorskii's work in view of the completion, on March 3, 1960, of one century since the birth of this distinguished chemist, who had a substantial influence on the development of some branches of organic chemistry. It must be emphasized that in the fifteen years that have passed since Favorskii's death (August 8, 1945) his scientific discoveries have acquired a still higher reputation and have received more extensive and varied application.

* V. I. Lenin. Collected Works [in Russian] (Inst. Marks-Lenina, 1947), Vol. 14, p. 91.

In this paper we examine the conditions for and the courses taken by intramolecular oxidation-reduction reactions; in particular, the mechanisms of the hydroxy-ketone and acid transformations of halo- and hydroxy-carbonyl compounds, including sugars.

Mechanism of the hydroxy-ketone rearrangement of hydroxy carbonyl compounds. The ketone transformation of aldehydes and ketones [2], which is allied to the hydroxy-ketone isomerization of hydroxy carbonyl compounds, is brought about by an acidic reagent (acids and hydrolyzable mercury, aluminum, and zinc salts), or by heterogeneous catalysis, or by heat, as a result of the mobility of a hydrogen in an aldehyde group or in a hydrocarbon residue on or adjacent to a carbonyl group. In the case of the hydroxy-ketone rearrangement of hydroxy carbonyl compounds in acidic and alkaline media the mobility of the hydrogen atoms of the alcohol and aldehyde groups, and also of the hydrocarbon residues, is also of significance. In the investigations of Danilov [5] and Venus-Danilova [6] syntheses of aliphatic and alicyclic α -monohydroxy aldehydes were carried out and these were isomerized into α -hydroxy ketones in a weakly acid medium and, in lower yields, in an alkaline medium (in the latter case other transformations readily occur). The isomerization of α -hydroxy ketones, discovered by Favorskii and co-workers [4], is characterized in the simplest case (e.g., the isomerization of 2-hydroxy-3-pentanone into 3-hydroxy-2-pentanone) by the displacement of both hydrogen atoms from the alcohol group to carbonyl. In α -hydroxy aldehydes and α -hydroxy ketones having a tertiary alcohol group migration of hydrocarbon residues is also observed. In such α -hydroxy aldehydes the hydrogen atom of the aldehyde group is displaced to the tertiary alcohol group, and one hydrocarbon residue to the place vacated. More complex displacements are peculiar to α -hydroxy aldehydes containing a secondary alcohol group. These displacements may be illustrated by the transformation of (benzyloxy)acetaldehyde into 1-hydroxy-1-phenylacetone, rather than into lactophenone [7]. Hence, in the hydroxy-ketone rearrangement of α -hydroxy carbonyl compounds there occurs intramolecular oxidation and reduction, sometimes in an obvious form, but sometimes in a less obvious form; this can be formulated in terms of electronic concepts of oxidation-reduction processes, as also in the isomerization of aldehydes and ketones into ketones.

The oxidation-reduction rearrangement of a molecule is characterized by the fact that one part of the molecule is oxidized; for this a movement of electrons onto the oxygen and carbon of the carbonyl group is characteristic. Another part of the molecule is found to be more reduced; onto this is displaced the hydrogen atom of the aldehyde group or the most electronegative (electron-accepting, electrophilic) hydrocarbon residue present in the molecule. In the neighborhood of the carbonyl is disposed the most electropositive (electron-donating, nucleophilic) hydrocarbon group, such as the electron-donating groups $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{CH}(\text{CH}_3)$, $\text{cis-C}_6\text{H}_{11}$. At the carbon adjacent to carbonyl is found a hydrogen atom or a phenyl group $-\text{C}_6\text{H}_5$, i.e., more negative (electron-accepting, electrophilic) groups. This is confirmed by the known examples of the isomerization of ketone into ketones and by most examples of the aldehyde-ketone rearrangement [2]. In the isomerization of some aldehydes from which two ketones may be formed, sometimes ketones capable of further isomerization and containing an electron-accepting group at the carbonyl are formed, or a mixture of two ketones may be formed, if H_2SO_4 does not bring about their isomerization. For example: 2,2-diphenylpropionaldehyde in concentrated sulfuric acid forms 2-phenylpropiophenone [2], which is capable of being isomerized, when heated to 330° with zinc chloride, to 1,1-diphenylacetone, in which there is a methyl group adjacent to the carbonyl.

Series of radicals arranged in order to electronegativity and electropositivity or, in an earlier form of expression, affinity were deduced by Danilov from the electric conductivities of acids in an examination of the course of the dehydration of α -glycols and the isomerization of aldehydes into ketones, which was published in his report for 1915 and appeared in the press in 1926 [8]. It is known [9] that this idea of making use of the electric conductivities of acids in judging the electronic properties of hydrocarbon residues (their electronegativities) found expression also in the works of other authors (Falk, Lewis, Lucas). According to Lewis and Lucas the removal of electrons from the α -carbon atom of an acid should increase the degree of ionization of the hydrogen atom of the carboxy group. In the dehydration of α -glycols, e.g., cyclohexylhydrobenzoin, under milder conditions there are obtained [2] mainly products in which intramolecular oxidation-reduction is less strongly marked: cyclohexyldiphenylacetaldehyde and cyclohexyldeoxybenzoin (and a little cyclohexyl diphenylmethyl ketone). As the conditions are made more severe (increase in the concentration of acid) one product begins to predominate, and with concentrated sulfuric acid this product, cyclohexyl diphenylmethyl ketone, is the only one obtained, i.e., around the carbonyl are disposed the electron-donating radicals which correspond to the weaker acid. In the isomerization of aldehydes of the cycloalkane series a leading role is played by the nature of the ring (according to the experiments of Venus-Danilova [6] ketones having five and six-membered rings are obtained).

The transformations of α -monohydroxy aldehydes and monohydroxy ketones also proceed so that the hydrocarbon residues CH_3 , C_2H_5 , etc., are arranged immediately in the vicinity of the carbonyl. Favorskii noted that in aliphatic ketones and hydroxy ketones the carbonyl tends to be displaced toward the end of the chain with the preferential formation of acetyl [2, 4]. This conclusion should be generalized for the series of radicals according to electrophilic character. In the isomerization of α -hydroxy carbonyl compounds the less electronegative hydrocarbon group comes adjacent to the carbonyl group. Unfortunately, up to now the isomerization of only a few α -hydroxy ketones and of very few α -hydroxy aldehydes with various substituents has been studied. In cyclic α -hydroxy aldehydes there is strain in the rings and they show the property of isomerization into hydroxy ketones in which both the alcohol group and carbonyl group are in the ring. In monohydroxy carbonyl compounds there are two reaction centers differing in degree of oxidation, and the stabilities of these depend on the electronic properties of the adjacent hydrocarbon residues and hydrogen atoms and on the displacement of the electron cloud to one part of the molecule toward the carbonyl.

The hydroxy-ketone transformation of α -hydroxy aldehydes and α -hydroxy ketones has an analogy in the long discovered epimerization of monoses [14] (Lobry de Bruyn and van Ekenstein) in presence of metal (calcium, barium, lead) hydroxides. It was later effected in an acid medium. The epimerization of aldoses into ketoses and back (glucose and fructose) was carried out for the first time without formation of mannose impurity in considerably higher yields by Danilov, Venus-Danilova, and Shantarovich [10] by heating the monose in dry pyridine and quinoline. It is noteworthy that in aqueous pyridine the reversible conversion of D-glucose into D-fructose is accompanied by the formation of mannose, which is usually obtained in the epimerization of D-glucose in presence of metal hydroxides. In the case of bioses (maltose) organic bases no longer bring about epimerization, but only anomeric changes [11]. The conversion of an α -hydroxy aldehyde grouping into a hydroxy ketone grouping by heating with pyridine has been described [12] in the steroid group. Under the same conditions diphenylglycolaldehyde does not form benzoin [5]. All this indicates the great specificity of reagents in the group of hydroxy carbonyl compounds. Lobry de Bruyn and van Ekenstein suggested that the epimerization of D-glucose passes through a cyclic form with an ethylene oxide ring, not previously described for monoses, i.e., through an α -hydroxy epoxy compound. It was here, and also independently by Favorskii [3], that an explanation was given for the acid conversion of monochloro ketones into acids via α -hydroxy epoxides, and later a similar explanation was given of the isomerization of α -hydroxy ketones [4]. It is known that the α -hydroxy epoxides can be obtained as their methyl derivatives (α -methoxy opoxides) [13].

Since the schemes of intermediate isomeric compounds are described in accordance with Butlerov's theory of structure, then irrespective of whether they are formed or are only assumed to be formed in the reaction medium, we may by making use of them, predict possible courses of the reaction. Hydroxy epoxy compounds, being intermediates according to Favorskii, were applied [5] with success to predict the hydroxy-ketone and acid transformation of α -hydroxy aldehydes (Danilov). However, further investigations showed the inadequacy of a scheme based on immediately formed α -hydroxy epoxides to represent the mechanism of the hydroxy-ketone transformation of α -hydroxy aldehydes. From α -hydroxy aldehydes having a secondary alcohol group we obtained isomeric α -hydroxy ketones which also had a secondary alcohol group (1-hydroxy-1-phenylacetone from α -hydroxyhydrocinnamaldehyde), but not a primary alcohol group, as would be expected from the α -hydroxy epoxide scheme [7]. Hydroxy ketones with a primary alcohol group are not isomerized [14] into keto alcohols with a secondary alcohol group, which are more reactive (initiation of polymerization, polarograms). The transformations of α -hydroxy aldehydes with secondary alcohol groups may be represented by a complex scheme (through an enediol with subsequent allyl rearrangement of an ethylenic alcohol). In this way we may represent the formation of a methyl group in the isomerization of 2-hydroxy-2-methylpropionaldehyde, 2-hydroxyheptanal, and α -hydroxyhydrocinnamaldehyde. The epimerization of monoses is sometimes represented as occurring with the supposed formation of an intermediate enediol with participation of the carbonyl group and the adjacent alcohol group. The interrelations of the hydroxy ketones 2-hydroxypropiophenone and 1-hydroxy-1-phenylacetone were explained in the same way by Favorskii and Temnikova [15], though the α -hydroxy epoxide scheme can be applied here. The formation of enediols may be brought about for some hydroxy carbonyl compounds, but for hydroxy ketones and hydroxy aldehydes having tertiary alcohol groups these schemes are inapplicable. For α -hydroxy aldehydes having secondary alcohol groups neither the α -hydroxy epoxy scheme nor the enediol scheme gives any indication that it is operative during the transformation into α -hydroxy ketones. There is no basis at all for the assumption of the intermediate formation of dimers of the acetal type in the epimerization of monoses; no-one has yet obtained any such compound for monoses [16].

It is usual to represent [17] the isomerization of aldehydes and ketones into ketones and of α -hydroxy aldehydes and α -hydroxy ketones into α -hydroxy ketones as being of the type of the pinacolone and retopinacolone rearrangements. This scheme is attractive for its generality and because of the introduction of electronic concepts in the

explanation of isomerizations in which a rearrangement of the carbon skeleton occurs. However, in these schemes the natures of the reacting molecules and of the reagent are, as it were, deprived of their individualities.

It may be supposed that hydrogen bonds may arise in hydroxy carbonyl compounds and the formation of these may be acknowledged as the start of an oxidation-reduction transformation. In themselves, hydrogen bonds form an example of simultaneous oxidation and reduction. The mobilities of hydrogen atoms and hydrocarbon residues are determined by the activating action of the reagent (acid and alkali) in the complex formed by the reagent with the hydroxy carbonyl compounds. In the rearrangement of molecules of hydroxy carbonyl compounds the phenomenon remains an intramolecular one; ions and radicals do not become isolated in accordance with the views of Lowry [18]. Experiments with labeled hydrogen and oxygen atoms in the reacting molecule and in the reagent may possibly determine whether the acid and base participate with their ions in the composition of the substances formed and whether hydrogen atoms and the hydroxyl of the carbonyl compound undergo exchange with these ions. It may be asserted that the reaction centers (the alcohol group or the carbonyl or both together) participate in the formation of the complex with the reagent.

The hydroxy-ketone rearrangement has a direct relation with reactions in which the halogen atom in halo carbonyl compounds is replaced by hydroxyl or an ester grouping. Halo carbonyl compounds in which the halogen plays the part of a second reaction center may be converted into hydroxy carbonyl compounds without rearrangement of the molecule as a result of direct replacement of the halogen atom by hydroxyl, or isomerization may occur with formation of an isomeric hydroxy carbonyl compound.

The higher reactivity of a halogen atom in comparison with hydroxyl is confirmed by the more ready isomerization in the hydrolysis of the halo carbonyl compound than in the direct isomerization of the hydroxy carbonyl compound. Thus, a keto alcohol with a primary alcohol group is not isomerized into another keto alcohol, but from 1-chloro-2-butanone in presence of lead hydroxide or silver oxide in a strongly alkaline medium at room temperature two isomeric keto alcohols were obtained: 3-hydroxy-2-butanone and 1-hydroxy-2-butanone [14]. This indicates that under certain specific conditions keto alcohols containing primary alcohol groupings may nevertheless be directly isomerized into a keto alcohol containing secondary alcohol groupings. The conversions of α -halo ketones corresponding to hydroxy ketones containing secondary and tertiary alcohol groupings into isomeric hydroxy ketones were first described [4] by Favorskii and co-workers.

Acid transformation of α -hydroxy and α -halo carbonyl compounds. The saccharinic rearrangement of aldoses and ketoses, which is a typical intramolecular oxidation-reduction reaction, has been known for a long time. The saccharinic (acid) rearrangement has been carried out for the first time also for aliphatic and [19] cyclic α -monohydroxy aldehydes containing a tertiary alcohol group in presence of lead and copper hydroxides (Danilov, Venus-Danilova). Thus, 2-hydroxy-2-methylpropionaldehyde is isomerized into isobutyric acid. For α -monohydroxy ketones and for α -hydroxy aldehydes having a secondary alcohol group, no such reaction has yet been found.

For the mechanism of the formation of saccharinic acids from monoses several schemes have been proposed which are fairly complex and have not been confirmed by direct experiments, for example the scheme of Nef and Isbell [20]. It is supposed that the reaction proceeds through various intermediate stages, which taken together amount to a type of benzil rearrangement. It is probable that the acid transformation of monoses, including ketoses, proceeds by the same mechanism as the conversion of α -hydroxy aldehydes into acids. In spite of the large extent of the literature, the question of the mechanism of the saccharinic rearrangement remains unelucidated. The rearrangement amounts in the main, to a displacement of hydroxy groups into the α - and β -positions and the formation of carboxyl. The acid transformation of α -monohydroxy aldehydes proceeds with the greatest yields under the specific action of copper and lead hydroxides in presence or absence of caustic alkali. Experiments showed that, in presence of caustic alkali only, 2-hydroxy-2-methylpropionaldehyde is converted by the Cannizzaro reaction into 2-methyl-1,2-propanediol and 2-hydroxy-2-methylpropionic acid. It is necessary only to introduce lead hydroxide into this medium for the reaction to take the direction of the formation of isobutyric acid in good yield. It should be noted that the active agents, lead hydroxide and copper hydroxide which readily combine with alkaline reagents in plumbites and amines, may behave both as alkaline and as acidic agents. This peculiarity of these hydroxides is probably of special significance in the oxidation-reduction transformations of hydroxy aldehydes into acids and in the partial formation in this of an α -hydroxy ketone.

The reaction of lead and copper hydroxides and of sodium plumbite with α -hydroxy aldehydes can be written down in different ways: 1) the hydroxide adds loosely to the aldehyde group without formation of any stable compound, and a hydrogen atom is displaced and the hydroxyl of the hydroxy aldehyde molecule moves to the carbonyl

with formation of the salt of an acid; 2) the hydroxide adds to the hydroxyl, not necessarily with formation of an alkoxide as stated by us previously [19], and this complex group moves over to the aldehyde group with displacement of a hydrogen atom. The metal hydroxide, in forming an unstable complex, has a substantial effect on the mobilities of the hydroxyl of the tertiary alcohol group and the hydrogen of the aldehyde group, and here the mutual effects of the hydrocarbon groups attached to carbons adjacent to carbonyl are in evidence. The electronic characteristics of the molecule in its static and particularly in its dynamic states and the electronic characteristics of the metal hydroxides are bound to manifest themselves [19].

The saccharinic rearrangement of monoses and α -hydroxy aldehydes greatly resembles the acid transformation of monohalo carbonyl compounds, though the mechanisms of these reactions must differ because of the specific properties of the halogen atom. In recent years, particularly in connection with steroid chemistry, Favorskii's rearrangement (acid transformation of aliphatic and alicyclic α -halo ketones) has become widely known [3]. The first example of the acid transformation of halo aldehydes was the conversion of chloral into dichloroacetic acid under the action of potassium cyanide (Wallach). Still earlier there is a brief reference (Maumene) to the same transformation of chloral in presence of silver oxide. However, Wallach and Favorskii [3] considered that this statement was doubtful. They considered it to be essential that the reagent should add to carbonyl, which was well known to be so in the case of potassium cyanide.

For a number of cases Danilov and Venus-Danilova [7] showed that α -halo aldehydes form almost quantitative yields of acids under the action of silver and lead hydroxides, whereas heating with barium carbonate leads to almost exclusive replacement of the halogen atom by hydroxyl. On being heated with lead hydroxide, 2-halo aldoses are converted into orthosaccharinic acids [21]. In Danilov's first paper on the isomerization of α -hydroxy aldehydes [5] the mechanism of the acid transformations of α -hydroxy and α -halo aldehydes was represented as proceeding through α -hydroxy epoxides in accordance with Favorskii. It was pointed out that the formation of heptanoic acid from bromoheptanal, which was observed by Kirmann [22], cannot be regarded as a result of an equilibrium between α -bromo aldehydes and acid bromides, as this author considered in his paper, which had only just appeared. It is more likely that here we have a transformation analogous to the Favorskii transformation of halo ketones. Kirmann later explained this transformation as occurring through a ketene.

The mechanism of the reactions in the Favorskii acid transformation of α -halo ketones is widely discussed in the literature. The following schemes have been most widely discussed for the mechanisms of the reactions occurring in the acid transformation of α -halo carbonyl compounds: 1) via α -hydroxy epoxides, which can exist in an alkaline medium; 2) via ketenes, whose formation has not been proved under the conditions under consideration. The transformations of most α -hydroxy ketones and α -hydroxy aldehydes can be represented as proceeding through α -hydroxy epoxides, but not all cases of such reactions can be fitted into the α -hydroxy epoxide scheme. Thus, in the acid transformation of 1-chloro-1-phenylacetone hydrocinnamic acid is formed, whereas the α -hydroxy epoxide scheme predicts the formation of 2-phenylpropionic acid. The conversion of α -halo aldehydes into acids can be represented as passing through ketenes, but for the acid transformation of α -halo ketones this scheme is either quite inapplicable (for tertiary and primary α -halo ketones) or conceivable only with great complications (for secondary halo ketones). Thus, the formation of butyric acid from 1-chloro-2-butanone and hydrocinnamic acid from 1-chloro-3-phenylacetone cannot be explained as occurring with the intermediate formation of a ketene. Of the recently proposed mechanisms for the acid transformation of α -halo ketones, Favorskii's electronic treatment of the reaction, called the benzil scheme, is of interest, and here the part played by alkali is noteworthy [23]. The rearrangement of α -halo carbonyl compounds appear to occur at the moment of the splitting of the halogen atom from the reagent in the complex formed by the carbonyl compound and the reagent by addition of the metal hydroxide to the carbonyl with displacement of a hydrogen atom or a radical to the carbon atom adjacent to the carbonyl. In the literature on the reaction of α -halo ketones with alkaline agents there are statements [24] to the effect that it begins with the carbon atom of the carbonyl group and is determined by the conjugation of the π -bonds with the C-OH bond that is forming and the C-Hal bond that is breaking down. It is supposed that the outgoing halogen atom and the incoming substituent are simultaneously bound with two carbon atoms—both with that which carried the halogen and with the carbon of the carbonyl group. The question of intermediate complexes still awaits detailed study.

Some new light on the saccharinic rearrangement and acid transformation of α -halo carbonyl compounds is thrown by recent work by Danilov, Anikeeva, and Lopatenok [25]. From this it follows that in halo carbonyl compounds the main course of the reaction is determined by the position of the halogen atom and that in α -hydroxy carbonyl compounds, apart from the first reaction center (the carbonyl group), there is a second reaction center, namely a hydroxyl in the α - and particularly in the β -position. When the α -chloro aldehyde 2-chloro-3-hydroxy-

propionaldehyde is treated with lead hydroxide, 3-hydroxypropionic acid, which is readily converted into acrylic acid, is formed. Under the same conditions 2,3-dihydroxypropionaldehyde gives lactic (2-hydroxypropionic) acid. In an alkaline medium α - and β -hydroxy epoxides may exist in the case of halo and polyhydroxy carbonyl compounds, so that the transformation of 2-chloro-3-hydroxypropionaldehyde can be represented as occurring through the α -hydroxy epoxide, and the conversion of 2,3-dihydroxypropionaldehyde under the action of lead hydroxide into lactic acid can be represented as occurring through the β -hydroxy epoxide. On the assumption that in monoses the carbonyl group has a strong inductive action on the α - and β -alcohol groups, a mechanism was presented for the formation of saccharinic acids from monoses via α - and β -hydroxy epoxides, depending on the structure of the monose; these are clearer and more probable schemes than those usually accepted, which originate from Nef and Isbell [20]. It may be thought that in monoses the mobilities of the hydroxy groups, the tendency of the alcohol groups of monoses to undergo dehydration and oxidation with Fehling's solution, etc., will vary according to the influence of the carbonyl group and the stereochemistry of the alcohol groups. It is probable that the induction effect of the carbonyl group or of the cyclic (pyranose, furanose) group favors a greater mobility of the hydroxyls of the secondary alcohol groups of monoses than in α -monohydroxy aldehydes with secondary alcohol groups, which are incapable of the saccharinic rearrangement (unlike the corresponding α -halo aldehydes).

The specific action of lead, silver, and copper hydroxides in the acid transformation of hydroxy and halo carbonyl compounds should be noted; it is probably associated with their ability to undergo complex formation and to exhibit basic and acidic properties simultaneously, specially in presence of alkali, which is due to the electron clouds and the nuclei of their atoms. The acid transformation of α -halo and α -hydroxy carbonyl compounds proceeds under conditions of pseudohomogeneous catalysis in accordance with the views of Semenov and co-workers [26]. They pointed out that the mechanisms of reactions occurring heterogeneously in a multimolecular adsorption film are analogous to the mechanisms of homogeneous catalytic reactions. By the isomerization of aldehydes into ketones in presence of mercury and other salts and by the part played by metal hydroxides in the transformations of halo and hydroxy carbonyl compounds it is undoubtedly confirmed that the catalytic activity of the salts and hydroxides of metals is associated with complex formation. Kobozev [27] also emphasizes, though on the basis of other theoretical considerations and experiments, the part played by complexes, with the condition that these complexes are highly unstable; he introduces the concept of "aggravation." Acid-alkali-salt catalysis plays an important part in reactions of simultaneous oxidation and reduction [28].

For the elucidation of the mechanisms of the reactions of organic compounds much purposeful work is required by organic and physical chemists with the extensive use of kinetic investigations and the modern methods of physics, and this forms the task in future investigations.

SUMMARY

1. In the isomerization of carbonyl and hydroxy carbonyl compounds by reactions of intramolecular oxidation and reduction, the most electropositive hydrocarbon group becomes attached at the carbonyl and the most electronegative group at the carbon atom adjacent to the carbonyl.
2. An explanation of the reaction mechanisms on the basis of the hypothesis of the role of unstable intermediate products meets with contradictions. The chief significance is to be given to the mobility of hydrogen atoms and hydrocarbon groups under the influence of neighboring groups and the reagent; the rearrangement occurs intramolecularly.
3. Specific effects were found for lead and copper hydroxides in the acid transformation of α -hydroxy and α -halo aldehydes and monoses, and for mercury salts in the aldehyde-ketone rearrangement.
4. The acid transformation of 2,3-dihydroxypropionaldehyde into lactic acid in presence of lead hydroxide can be represented as passing through a β -hydroxy epoxide, but the transformation of 2-chloro-3-hydroxypropionaldehyde into 3-hydroxypropionic acid—as passing through an α -hydroxy epoxide. The saccharinic rearrangement of monoses results from the mobility of hydroxy groups with passage through the stage of α - and β -hydroxy epoxides.

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MIXED PHOSPHOROUS ESTERS DERIVED
FROM DIETHYL D-TARTRATE

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By the action of diethyl tartrate on Menshutkin acid chlorides (alkyl phosphorodichloridites) in presence of bases we obtained mixed phosphorous esters, namely the methyl, ethyl, propyl, butyl, and allyl esters shown in Table 1. Some of their properties were studied [1, 2].

TABLE 1

Formula	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	MR		$[\alpha]_D^{20}$ in absence of solvent	$[\alpha]_D^{20}$ in benzene solution
				found	calc.		
$\begin{array}{c} \text{COOC}_2\text{H}_5 \\ \\ \text{CHO} \diagup \text{P-OCH}_3 \\ \\ \text{CHO} \diagdown \\ \\ \text{COOC}_2\text{H}_5 \end{array}$	129-130 (2,5)	1,2439	1,4525	57,74	57,93	-96,47°	-80,88°
$\begin{array}{c} \text{COOC}_2\text{H}_5 \\ \\ \text{CHO} \diagup \text{P-OC}_2\text{H}_5 \\ \\ \text{CHO} \diagdown \\ \\ \text{COOC}_2\text{H}_5 \end{array}$	132-133 (2)	1,2036	1,4500	62,70	62,55	-95,85°	-77,93°
$\begin{array}{c} \text{COOC}_2\text{H}_5 \\ \\ \text{CHO} \diagup \text{P-OC}_3\text{H}_7-n \\ \\ \text{CHO} \diagdown \\ \\ \text{COOC}_2\text{H}_5 \end{array}$	137-138 (3,5)	1,1745	1,4505	67,36	67,27	-93,65°	-75,9°
$\begin{array}{c} \text{COOC}_2\text{H}_5 \\ \\ \text{CHO} \diagup \text{P-OC}_4\text{H}_9-n \\ \\ \text{CHO} \diagdown \\ \\ \text{COOC}_2\text{H}_5 \end{array}$	143,5-144 (1-1,5)	1,1511	1,4500	71,94	71,88	-89,18°	-73,05°
$\begin{array}{c} \text{COOC}_2\text{H}_5 \\ \\ \text{CHO} \diagup \text{P-OC}_3\text{H}_5 \\ \\ \text{CHO} \diagdown \\ \\ \text{COOC}_2\text{H}_5 \end{array}$	136-137 (1,5)	1,2003	1,4600	66,66	66,70	-91,72°	-74,8°

*For the determination of rotation solutions of about 20% strength were taken.

TABLE 2

Formula	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	MR		$[\alpha]_D^{20}$
				found	calc.	
$\begin{array}{c} \text{COOC}_2\text{H}_5 \\ \\ \text{CHO} \diagup \text{P} \diagdown \text{S} \\ \quad \quad \quad \\ \text{CHO} \quad \quad \quad \text{OCH}_3 \\ \\ \text{COOC}_2\text{H}_5 \\ \\ \text{COOC}_2\text{H}_5 \end{array}$	163—164 (4—4,5)	1,3048	1,4695	63,51	64,35	—56,6°
$\begin{array}{c} \text{CHO} \diagup \text{P} \diagdown \text{S} \\ \quad \quad \quad \\ \text{CHO} \quad \quad \quad \text{OC}_2\text{H}_5 \\ \\ \text{COOC}_2\text{H}_5 \\ \\ \text{COOC}_2\text{H}_5 \end{array}$	159—160 (3,5)	1,2603	1,4680	68,82	68,97	—57, 1°
$\begin{array}{c} \text{CHO} \diagup \text{P} \diagdown \text{S} \\ \quad \quad \quad \\ \text{CHO} \quad \quad \quad \text{OC}_3\text{H}_7-n \\ \\ \text{COOC}_2\text{H}_5 \\ \\ \text{COOC}_2\text{H}_5 \end{array}$	158—160 (1,5—2)	1,2282	1,4685	73,83	73,58	—38,43°
$\begin{array}{c} \text{CHO} \diagup \text{P} \diagdown \text{S} \\ \quad \quad \quad \\ \text{CHO} \quad \quad \quad \text{OC}_4\text{H}_9-n \\ \\ \text{COOC}_2\text{H}_5 \\ \\ \text{COOC}_2\text{H}_5 \end{array}$	177—178 (3,5)	1,2060	1,4690	78,56	78,19	—36,74°
$\begin{array}{c} \text{CHO} \diagup \text{P} \diagdown \text{S} \\ \quad \quad \quad \\ \text{CHO} \quad \quad \quad \text{OC}_3\text{H}_5 \\ \\ \text{COOC}_2\text{H}_5 \end{array}$	170—172 (2)	1,2670	1,4723	71,69	73,11	—38,7°

*The rotation was determined in absence of solvent in a cell 5 cm in length and 2.5 mm in diameter.

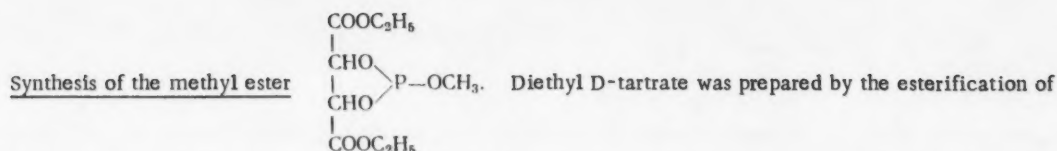
All the compounds obtained were optically active (levorotatory); they are thick colorless liquids with a feeble specific odor. Being compounds of trivalent phosphorus, mixed esters of phosphorous acid and diethyl D-tartrate react with cuprous salts with evolution of heat with formation of thick noncrystallizing syrups. Like phosphorous esters studied previously, those now synthesized by us undergo addition of sulfur with formation of the corresponding phosphorothioic esters.

We obtained the following cyclic phosphorothioic esters (Table 2).

The cyclic phosphorous esters obtained react in a complicated way with alkyl and acyl halides. Thus, in the reaction of the ethyl ester with ethyl iodide (heating at 150° for seven hours) we succeeded in isolating and identifying diethyl furmarate. In the reaction of the methyl ester with methyl iodide at 80–85° we again isolated a small amount of diethyl fumarate together with a little of an isomerization product of the mixed methyl phosphite taken (the product was impure). The bulk of the products of the reaction of cyclic ethyl and methyl phosphites with alkyl halides could not be distilled without decomposition and consisted of thick polymerized masses of dark-yellow or brown color. In all other cases no individual substances could be isolated.

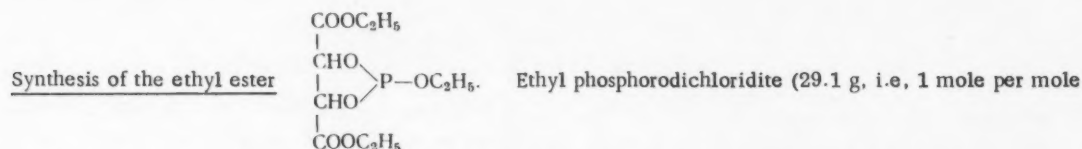
In reactions with bromotriphenylmethane the esters formed crystalline products containing halogen. Two products were isolated in the pure state: product of the reaction of the mixed cyclic ethyl phosphite with $(\text{C}_6\text{H}_5)_3\text{CBr}$, m.p. 162–163°, and product of the reaction of the propyl ester with $(\text{C}_6\text{H}_5)_3\text{CBr}$, m.p. 145.5–147°. On hydrolysis of the latter with 1 : 1 hydrochloric acid, triphenylmethylphosphonic acid was isolated.

EXPERIMENTAL

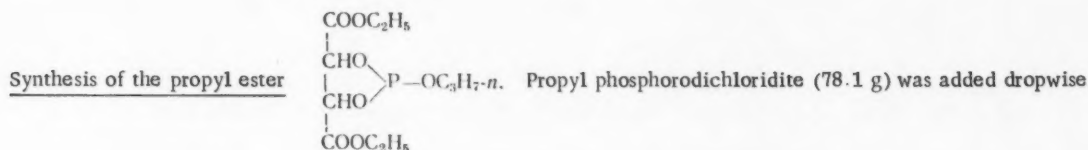


D-tartaric acid ($[\alpha]_D$ of a 20% aqueous solution of D-tartaric acid: $+12.4^\circ$); its constants: b.p. $126-127^\circ$ (2 mm); n_D^{20} 1.4445; $[\alpha]_D +9.56$. The literature gives: b.p. 137° (5 mm); 148° (9 mm); n_D^{20} 1.4445; $[\alpha]_D +9.30^\circ$.

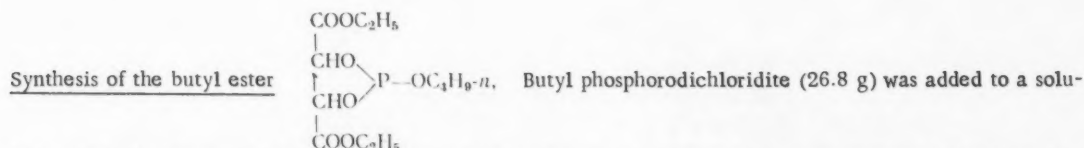
Methyl phosphorodichloridite (55 g diluted with one-half the amount of dry ether) was added dropwise over a period of one hour to a mixture of 86.5 g of diethyl D-tartrate, 83.67 g of triethylamine, and 550 ml of dry ether. When reaction ceased, triethylamine hydrochloride was filtered off and washed several times with ether. The filtrate was fractionally distilled. Three vacuum distillations gave a colorless oil of unpleasant odor, b.p. $129-130^\circ$ (2.5 mm), in an amount of 60.2 g (54.7%); d_4^{20} 1.2439; n_D^{20} 1.4525; found MR 57.74, calculated MR 57.93; $[\alpha]_D^{20}$ -96.47. Found: P 11.73; 11.77%. $\text{C}_9\text{H}_{15}\text{O}_7\text{P}$. Calculated: P 11.64%.



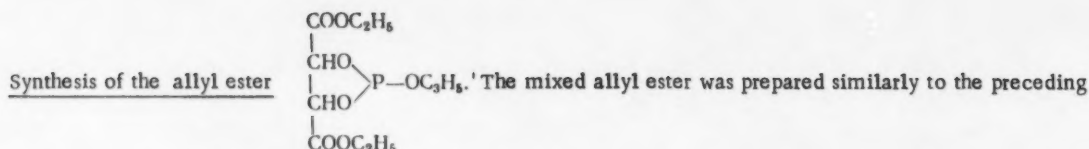
of diethyl D-tartrate) was added dropwise to a solution of 41.8 g of diethyl D-tartrate and 31.6 g of dry pyridine in 200 ml of dry ether under cooling with snow and salt. The precipitated pyridine hydrochloride was filtered off, and the filtrate was vacuum-distilled. Three distillations from an Arbuzov flask gave 37.5 g (about 85%) of a colorless liquid, which was more mobile than the methyl ester; b.p. $132-133^\circ$ (2 mm); d_4^{20} 1.2036; n_D^{20} 1.4500; found MR 62.70; calculated MR 62.55; $[\alpha]_D^{20}$ -95-85. The substance reacts with CuI at high temperature with formation of a thick syrup. Found: P 11.28%. $\text{C}_{10}\text{H}_{17}\text{O}_7\text{P}$. Calculated: P 11.06%.



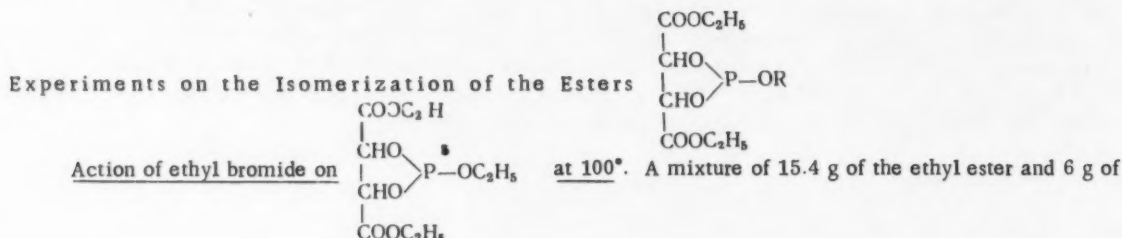
over a period of 90 min to a mixture of 102 g of diethyl D-tartrate, 77.1 g of dry pyridine, and 300 ml of dry ether under cooling with snow and salt. When the whole of the acid chloride had been added, the reaction mixture was stirred for 30 min. Pyridine hydrochloride was filtered off, and filtrate was twice fractionated from an Arbuzov flask under reduced pressure. We obtained 102.3 g (71.3%) of a colorless oil; b.p. $137-138^\circ$ (3.5 mm); d_4^{20} 1.1745; n_D^{20} 1.4505; found MR 67.36; calculated MR 67.27; $[\alpha]_D^{20}$ -93.65°. It reacted with CuI with formation of a thick syrup. Found: P 10.66; 10.69%. $\text{C}_{11}\text{H}_{19}\text{O}_7\text{P}$. Calculated: P 10.53%. The molecular weight determined cryoscopically in benzene was 291.4 (calculated value 294.15).



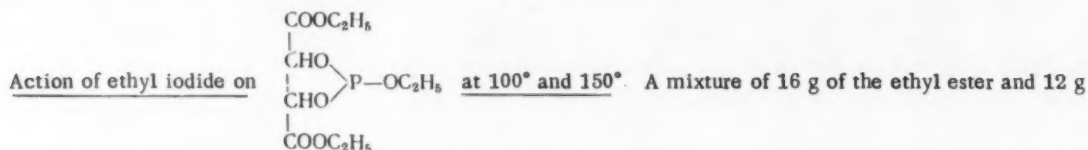
tion of 33 g of diethyl D-tartrate and 31.9 g of triethylamine in 200 ml of dry ether under cooling with snow and ice. After the usual treatment of the reaction products we obtained 31 g (63.7%) of a thick colorless liquid with a faint odor of butyl alcohol; b.p. $143.5-144^\circ$ (1.5-1 mm); d_4^{20} 1.1511; n_D^{20} 1.4500; found MR 71.94; calculated MR 71.88; $[\alpha]_D^{20}$ -89.18°. It reacted with cuprous halides. Found: P 9.92%. $\text{C}_{12}\text{H}_{21}\text{O}_7\text{P}$. Calculated: P 10.05%.



phosphorous esters. For reaction we took: 50.9 g of diethyl D-tartrate, 38.7 g of allyl phosphorodichloridite, and 49.2 g of triethylamine. We obtained 37.2 g (51.8%) of product; b.p. 136-137° (1.5 mm); d_4^{20} 1.2003; n_D^{20} 1.4600; found MR 66.66; calculated MR 66.70; $[\alpha]_D^{20}$ -91.72°. The product was similar in appearance to the above-described esters; it had the peculiar odor of allyl compounds. Found: P 10.60; 10.57%. $\text{C}_{11}\text{H}_{17}\text{O}_7\text{P}$. Calculated: P 10.5%



ethyl bromide (equimolecular amounts) was heated in a sealed tube at 100° for 10 hr. After the heating there was no change in the volume of the mixture. From the mixture we distilled 3.5 g of ethyl bromide (b.p. 38-41°). Residual ethyl bromide was removed in a vacuum. The weight of the residual mass was about 16 g. Vacuum distillation gave: Fraction I (0.5 g), b.p. 110-126° (3 mm) and n_D^{20} 1.4430; Fraction II (12 g), b.p. 126-129° (3 mm) and n_D^{20} 1.4502. Hence, under these conditions the reaction did not go.



of ethyl iodide was heated in a sealed tube at 100° for ten hours. No change in the volume of the mixture was observed. The contents of the tube remained colorless. The reaction was considered to be incomplete.

The same amounts of reactants were heated at 150° for seven hours. After the heating the mixture was slightly colored with iodine; its volume had increased slightly. By heating the mixture in a water bath we drove off 4 g of ethyl iodide, and under somewhat reduced pressure we removed a further 4.5 g of ethyl iodide.

The residue was distilled at 4-5 mm. We obtained two fractions: Fraction I, b.p. 84-85° (4.5-5 mm) and n_D^{20} 1.4393; Fraction II, b.p. 85° (4.5-5 mm) and n_D^{20} 1.4385; in all 5.52 g. When the flask was heated further there was severe decomposition and the residual pressure rose to 12 mm. A very thick, clear, dark-yellow liquid remained in the flask. Redistillation of Fractions I and II gave: Fraction I (0.5 g), b.p. 63.5-65.5° (2.5 mm) and n_D^{20} 1.4380; Fraction II (4.6 g), b.p. 65.5-66.5° (2.5 mm), n_D^{20} 1.4390, and d_4^{20} 1.0523.

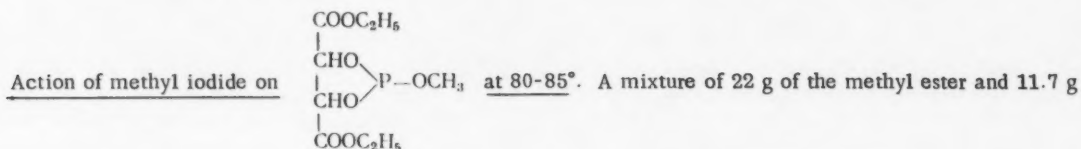
The product was a colorless mobile liquid with a feeble pleasant odor; it did not contain phosphorus. Found: C 55.52; 55.46; H 7.13; 7.11%. $\text{C}_8\text{H}_{12}\text{O}_4$. Calculated: C 55.78; H 7.02%. The molecular weight determined cryoscopically in benzene was 163.6.

Hence, as a result of the reaction we obtained fumaric ester, for which the literature gives: b.p. 98-99° (14 mm); n_D^{20} 1.4410; d_4^{20} 1.0535; mol. wt. 172.06.

Hydrolysis of the product of b.p. 65.5-66.5° (2.5 mm): A mixture of 0.5 g of the substance and 10 ml of 1 : 1 hydrochloric acid was refluxed for two hours. The precipitate formed was filtered off and crystallized from hot water (+ activated charcoal). We obtained 0.4 g of prisms, m.p. about 240° in a sealed capillary; in a metal block the crystals melted at about 260-270°. For fumaric acid the literature gives m.p. about 286° in a sealed capillary.

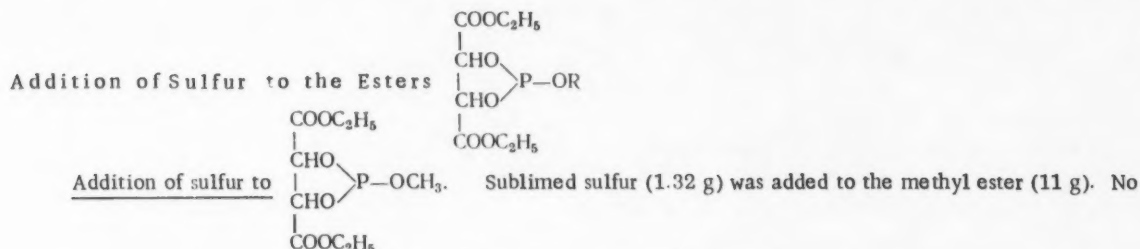
Preparation of dimethyl fumarate: 0.4 g of the substance obtained on hydrolysis of the ester was dissolved in 10 ml of absolute methanol. Hydrogen chloride was passed through the solution to saturation. The contents of the test tube rapidly solidified. We filtered off 0.2 g of crystals, m.p. 105-107° (from methanol). For dimethyl fumarate the literature gives m.p. 105-107°.

Preparation of fumaramide: A mixture of 1 g of the product of m.p. 65.5-66.5° (2.5 mm) and 7 ml of concentrated ammonia solution was left in a small flask at room temperature overnight. The precipitate formed was filtered off and crystallized from hot water. We obtained 0.67 g of a substance of m.p. about 270° (decomp.). For fumaramide the literature gives m.p. 265-270°.

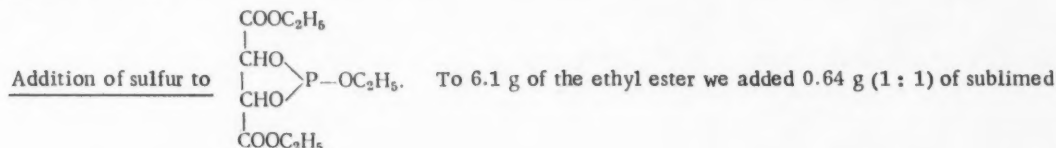


of methyl iodide was heated in a sealed tube at 80-85° for ten hours (until the mixture took up a faint yellow color). The volume of the mixture diminished somewhat. On fractionation of the reaction products we isolated 3.75 g of diethyl fumarate, b.p. 75-76° (7 mm), d_4^{20} 1.0521, and n_D^{20} 1.4392, and 4.1 g of a product having: b.p. 164-166° (2-2.5 mm); d_4^{20} 1.2985; n_D^{20} 1.4495; found MR 55.02; calculated MR 55.73. Found: P 12.00; 12.10%. $\text{C}_9\text{H}_5\text{O}_7\text{P}$. Calculated: P 11.64%.

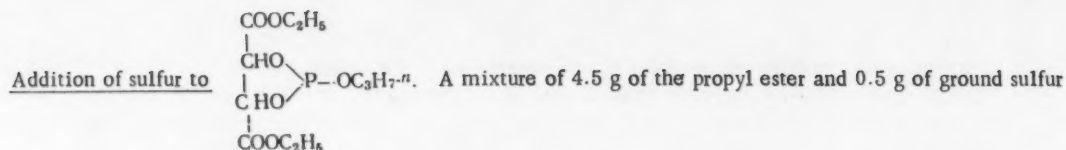
According to the analytical results the high-boiling product was probably an impure isomerization product of the mixed phosphorous ester of methanol and diethyl D-tartrate. A large residue of thick nondistillable dark-colored material remained in the flask.



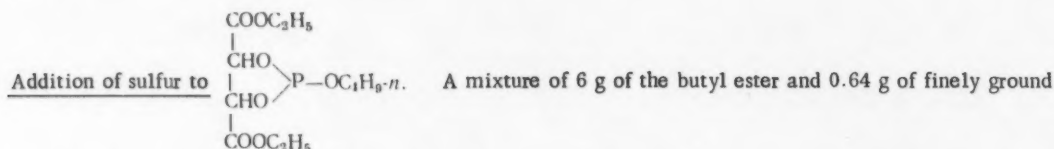
reaction occurred in absence of heat. When the mixture was heated to 130° an exothermic reaction set in, and much of the sulfur reacted with the ester. The reaction product was distilled twice from an Arbuzov flask. We obtained 5.71 g of a thick colorless liquid with an unpleasant odor of sulfur compounds; b.p. 163-164° (4-4.5 mm); d_4^{20} 1.3048; n_D^{20} 1.4695; found MR 63.51; calculated MR 64.35; $[\alpha]_D^{20}$ -56.6°. Found: S 10.44%. $\text{C}_9\text{H}_{15}\text{O}_7\text{PS}$. Calculated: S 10.75%.



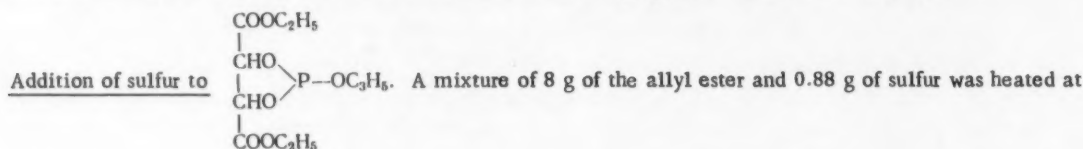
sulfur. As in the first case there was no reaction in absence of heating. At about 150° much of the sulfur dissolved in the ester. Distillation of the reaction product gave 4.1 g of a thick colorless liquid with a feeble unpleasant odor; b.p. 159-160° (3.5 mm); d_4^{20} 1.2603; n_D^{20} 1.4680; found MR 68.82; calculated MR 68.97; $[\alpha]_D^{20}$ -37.61°. Found: P 10.02; 9.99; S 9.67; 9.72%. $\text{C}_{10}\text{H}_{17}\text{O}_7\text{PS}$. Calculated: P 9.92; S 10.27%.



was heated in an Arbuzov flask at 160°. On vacuum distillation of the reaction products we obtained 3 g of a substance; b.p. 158-160° (1.5-2 mm); n_D^{20} 1.4685; d_4^{20} 1.2282; found MR 73.83; calculated MR 73.58; $[\alpha]_D^{20}$ -38.43°. It was similar in appearance to the preceding thio ester. Found: P 9.75; 9.65; S 9.36%. $\text{C}_{11}\text{H}_{19}\text{O}_7\text{PS}$. Calculated: P 9.50; S 9.83%.

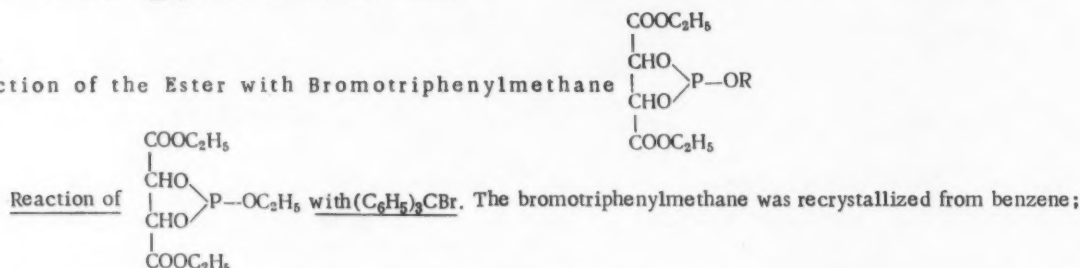


sulfur was heated in an Arbuzov flask at 160-170° until almost all the sulfur dissolved. Two distillations gave 4.5 g of a thick slight yellowish liquid with an unpleasant odor; b.p. 177-178° (3.5 mm); d_4^{20} 1.2060; n_D^{20} 1.4690; found: MR 78.56; calculated MR 78.19; $[\alpha]_D^{20}$ -36.74. Found: P 9.23%. $\text{C}_{12}\text{H}_{21}\text{O}_7\text{PS}$. Calculated: P 9.11%.

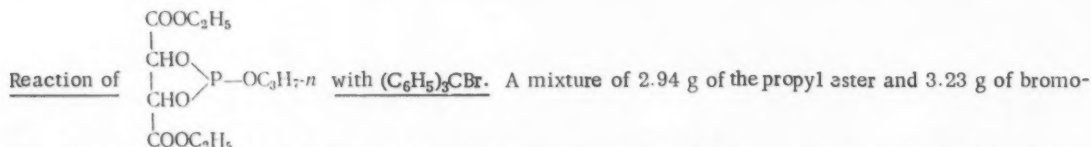


160-170° for 20 min. Fractionation of the reaction mixture gave 4.07 g of product; b.p. 170-172° (2 mm); d_4^{20} 1.2670; n_D^{20} 1.4723; found MR 71.69; calculated MR 73.11; $[\alpha]_D^{20}$ -38.7°. The substance had a strong garlic odor. Found: S 9.39%. $\text{C}_{11}\text{H}_{17}\text{O}_7\text{PS}$. Calculated: S 9.89%.

Reaction of the Ester with Bromotriphenylmethane



m.p. 150-153°. A mixture of 1.4 g of the ester and 1.6 g of $(\text{C}_6\text{H}_5)_3\text{CBr}$ (equimolecular amounts) was refluxed in dry benzene solution for one hour. This gave a homogeneous yellow solution. When this was boiled with activated charcoal, an almost colorless filtrate was obtained. On addition of hexane to this, colorless crystals were precipitated. Filtration gave 0.5 g of crystals, m.p. 162-163° (after recrystallization from methanol). Found: P 5.00; Br 13.03%. $\text{C}_{29}\text{H}_{32}\text{O}_7\text{PBr}$. Calculated: P 5.13; Br 13.24%.



triphenylmethane was refluxed in 10 ml of dry xylene for 90 min. Part of the solvent was distilled off, and 5 ml of petroleum ether was added to the residue. The precipitate formed was filtered off and recrystallized from a 2 : 1 alcohol-water mixture. We obtained 1.8 g of colorless fine needles, m.p. 145.5-147°, readily soluble in benzene, chloroform, acetone, and alcohols, but insoluble in water. Found: C 58.34; H 5.67; P 5.15; Br 12.90%. $\text{C}_{30}\text{H}_{34}\text{O}_7\text{PBr}$. Calculated: C 58.32; H 5.55; P 5.02; Br 12.94%. The molecular weight, determined by the Rast method, was 620.1; the value calculated for $\text{C}_{30}\text{H}_{34}\text{O}_7\text{PBr}$ is 617.18.

Hydrolysis of the product of m.p. 145.5-147°: A mixture of 0.2 g of the product and 10 ml of 15% hydrochloric acid was heated in a sealed tube at 180-185° for 8.5 hr. Needles of triphenylmethylphosphonic acid, m.p. about 275°, were filtered off.

SUMMARY

Mixed methyl, ethyl, propyl, butyl, and allyl esters of the acid ester formed by phosphorous acid with diethyl D-tartrate were synthesized, and some of their properties were studied.

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ORGANOPHOSPHORUS DERIVATIVES OF ETHYLENIMINE

COMMUNICATION 3. ADDITION OF CARBOXYLIC ACIDS

TO DIETHYL N-ETHYLENEPHOSPHORAMIDATE

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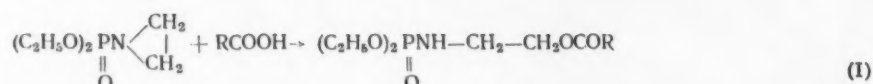
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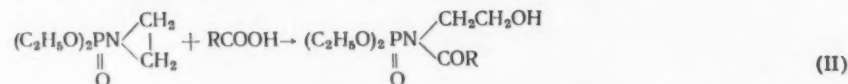
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In previous investigations [1, 2] we have shown that the ethyleneamides of phosphorus acids add to various substances with opening of the ethylenimine ring. All these reactions can be named satisfactorily by means of one general term: (dialkoxyposphinylidynamino)ethylation. In the present paper we give the results of the (diethoxyphosphinylidynamino)ethylation of carboxylic acids.

The reaction between diethyl N-ethylenephosphoramidate and carboxylic acids may be expressed by the equation:



Another, less preferable, but formally possible course of the reaction is:

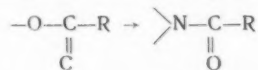


We obtained the products of the addition of diethyl N-ethylenephosphoramidate to various carboxylic acids; the results are given in the table.

To some extent, the question of the structure of the compounds obtained remained unresolved. It will be seen from the table that in the great majority of cases the discrepancy between the found and calculated values of molecular refraction speaks in favor of structure (II). However, not all reactions for hydroxyl gave positive results (with benzoyl chloride, phthalic anhydride, and 1-naphthyl isocyanate).

Several papers have appeared in the literature on the migration of an acyl group from oxygen to nitrogen in benzoic esters of amino alcohols. Clapp and co-workers [3] have shown that, when the opening of the ring of 2,2-dimethylethylenimine and 2-ethylethylenimine is carried out in neutral and alkaline media, only benzamido alcohols are obtained. Amino benzoates are formed only in an acid medium in the form of the corresponding salts. Analogous results were obtained earlier by van Tamelen [4] and by Fodor and Kiss [5].

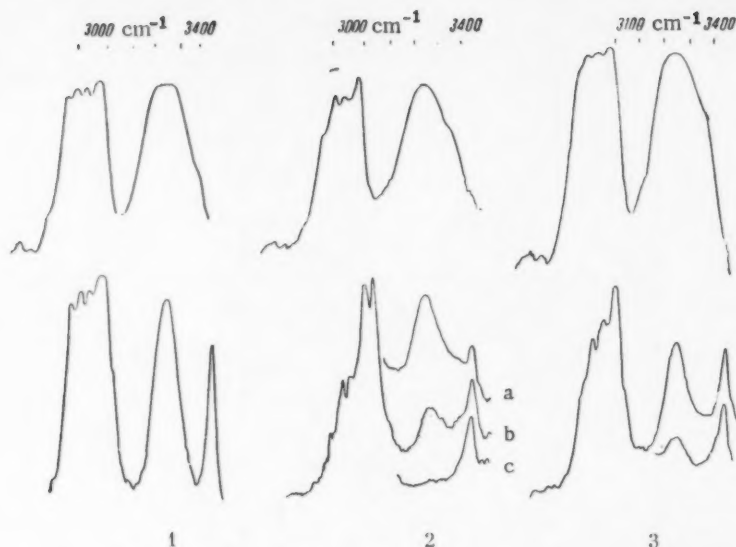
In our case the possibility of similar migration is not very probably because the nitrogen atom belongs to an



amide group that is fairly well screened with a phosphonic radical. However, the direct formation of a substance of structure (II) can formally occur.

For the final elucidation of the structures of the compounds obtained we studied the infrared absorption spectra of the products of the reaction of diethyl N-ethylenephosphoramidate with acetic and propionic acids. As a model compound we took diethyl N-ethylphosphoramidate. It was desirable to obtain also diethyl N-ethyl-N-2-hydroxyethylphosphoramidate as a model compound, but attempts to synthesize it by the action of ethylene oxide on diethyl N-ethylphosphoramidate and also by the action of 2-bromoethanol on the sodium derivative of diethyl

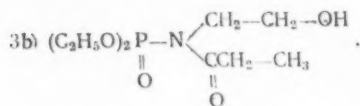
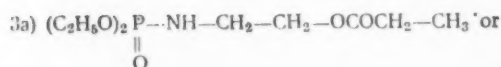
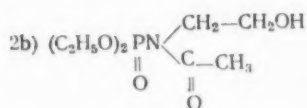
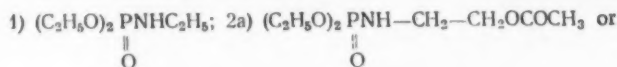
Formula [R = (C ₂ H ₅ O) ₂ PNH-CH ₂ -CH ₂ -] O	B. p. in °C (p in mm)	n _D ²⁰	d ₄ ²⁰	Calc. MR		Calc. MR	p %		Yield, (%)
				structure (I)	structure (II)		calc.	found	
R-OGCH ₃	152—153 (4,5)	1,4392	1,1509	55,00	54,88	54,65	12,97	12,68	59
R-OCOCH ₂ -CH ₃	147—150 (2,0)	1,4998	1,1245	59,62	59,50	59,30	12,26	12,22	58
R-OCO(CH ₂) ₂ CH ₃	145—146 (1,0)	1,4401	1,1009	64,23	64,11	63,93	11,61	11,39	60
R-OCOCH(CH ₃) ₂	134—136 (1,0)	1,4384	1,0935	64,23	64,11	64,10	11,61	11,37	58
R-OCOCH ₂ -CH(CH ₃) ₂	140—142 (1,0)	1,4398	1,0727	68,85	68,73	69,01	P 11,04 C 46,98 H 8,54	11,00 47,09 8,65	56
R-OCO(CH ₂) ₄ CH ₃	153—154 (1,0)	1,4418	1,0660	73,45	73,33	73,17	10,51 P 10,21 C 51,82	10,56 10,30 51,57	58
R-OCOC ₄ H ₉	Crystals	M. p. 44—47°					H 6,04 P 19,55 C 37,85	6,44 19,20 37,60	70—80
R-P(OC ₂ H ₅) ₂	168—171 (1,5)	1,4452	1,1603	72,94	72,82	72,78	H 7,88	7,91	47,5



Note: In the case of the spectrograms of substances (2) and (3) the curves (a), (b), and (c) refer to various diminishing concentrations; the upper curves are spectrograms of the pure substances; the lower curves are spectrograms of these substances in carbon tetrachloride.

N-ethylphosphoramidate were not successful. In the last case an exchange reaction occurs with formation of sodium 2-bromoethoxide and regeneration of the amide.

Above we give the spectrograms in the region $2300\text{--}3600\text{ cm}^{-1}$ for all three of the compounds indicated:



As will be seen from the spectrograms of the pure substances in the region of $2300\text{--}3600\text{ cm}^{-1}$, apart from the band of CH valence vibrations, all three compounds have a wide band with a maximum at 3220 cm^{-1} and a "shoulder" at 3365 cm^{-1} for (2) and (3) and at 3400 cm^{-1} for (1). The character and intensity of this band are such that there can be no doubt that it belongs to OH or NH valence vibrations. The resemblance of the spectra of (2) and (3) with that of the "model" compound, while favoring the structure (I), is still not a convincing proof and does not exclude the possibility that the band at 3220 cm^{-1} should be attributed to the vibrations of a bound OH group.

To obtain further information we determined the spectra of solutions of the substances under study in carbon tetrachloride. As will be seen from the spectrograms, in the spectra of dilute solutions of all three compounds there appears a new, much narrower band with maximum absorption at 3438 cm^{-1} . This band does not belong to the solvent. As the solution is diluted, the band at 3220 cm^{-1} and its shoulder gradually fall in intensity and then

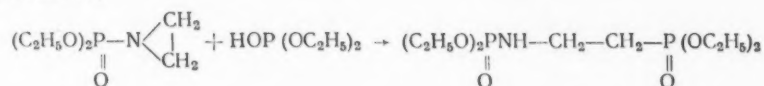
completely disappear, but the band at 3438 cm^{-1} increases in intensity. From this it is quite clear that the first belongs to the vibrations of a bound group and the second to the vibrations of a free group. In accordance with numerous data in the literature [6], the region of the frequencies of the valence vibrations of the free OH group is $3500\text{--}3700\text{ cm}^{-1}$. It is in the region of $3300\text{--}3500\text{ cm}^{-1}$ that the vibrations of the free NH group of secondary amides and amines appear [6]. Hence, the frequency of the vibrations of this free group, together with the analogy in behavior between corresponding regions of the spectra of the "model" compound and the compound under investigation, permits us to attribute the structure (I) to the latter with complete certainty. The lower-frequency regions of the spectra are also in accord with this conclusion. The vibration frequency of the C = O group in the molecules of (2) and (3) is at 1734 cm^{-1} for the pure substances and is displaced to 1750 cm^{-1} in the spectra of dilute solutions, i.e., it is higher than for ketones ($1706\text{--}1720\text{ cm}^{-1}$), to which the structure (II) is closer, and practically falls in the region of the vibration frequencies of C = O for normal saturated esters ($1735\text{--}1750\text{ cm}^{-1}$) [6], as would be expected for the structure (I).

The above-mentioned displacement of the vibration frequencies of the C = O group by 16 cm^{-1} , together with an analogous effect for the vibration frequencies of P = O (1236 cm^{-1} in the spectra of all three compounds for the pure liquids and about 1250 cm^{-1} in dilute solution) indicates that the compounds investigated contain both

$> \text{N-H} \dots \text{O} = \text{P} \begin{array}{l} \diagup \\ \diagdown \end{array}$ and $> \text{NH} \dots \text{O} = \text{C} <$ intermolecular bonds. On the basis of the spectrum of the "model" compound, in which the C = O group is absent, it is quite natural to attribute the main band at 3220 cm^{-1} to vibrations in the associated grouping $> \text{NH} \dots \text{O} = \text{P} \begin{array}{l} \diagup \\ \diagdown \end{array}$, and the "shoulder" at 3365 cm^{-1} in the spectra of (2) and (3) to vibrations of NH bound to C = O. The "shoulder" at 3400 cm^{-1} in the spectrum of (1) probably indicates that part of the NH bonds, which are occupied in (2) and (3) in the associated groupings $> \text{NH} \dots \text{O} = \text{C} <$, in this case remain free. The very high value (218 cm^{-1}) of the displacement of the vibration frequency of the NH group attached to P = O from the frequencies of the vibrations of the free group must be noted.

Hence, study of the infrared absorption spectra permits us to resolve the question of the structure of the compounds under investigation. All the peculiar features of the spectra in the region of 3000 cm^{-1} can also be interpreted in accord with the structure (I).

The question of the structure of the substance obtained by the action of diethyl hydrogen phosphite on diethyl N-ethylenephosphoramidate remained open. The elementary analysis corresponded to the substance which would be expected to be obtained:



The calculated and found molecular refractions were also in good agreement with the formula given. However, on hydrolysis of the substance we did not isolate 2-aminoethylphosphonic acid, which should have been formed if the above structure were correct. With the object of determining the structure a study of the infrared absorption spectrum of the compound was undertaken.

EXPERIMENTAL

All the derivatives of N-phosphonated 2-aminoethanol esters of carboxylic acids given in the table were prepared similarly. Equimolecular amounts of diethyl N-ethylenephosphoramidate and the carboxylic acid were heated together in sealed tubes for 6-7 hr at $110\text{--}120^\circ$. The pure substance was isolated after two distillations. The yields and constants of the compounds are given in the table. The infrared absorption spectrograms were obtained with an ISK-12 spectrometer with variable slit width; with a NaCl prism in the region $700\text{--}2400\text{ cm}^{-1}$ and with a LiF prism in the region $2300\text{--}3600\text{ cm}^{-1}$.

SUMMARY

1. By the action of carboxylic acids on diethyl N-ethylenephosphoramidate seven derivatives of N-phosphonated 2-aminoethanol esters of carboxylic acids were obtained.

2. The interpretation of the peculiar features of the infrared spectra leads to conclusion that intermolecular hydrogen bonds are present between the hydrogen of the amide group, on the one hand, and the oxygens of the phosphono group (P = O) and the ester group (C = O), on the other.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

SYNTHESIS OF UNSATURATED ORGANOSILICON COMPOUNDS BY THE DEHYDROCHLORINATION OF CHLORO(3-CHLOROALKYL)SILANES

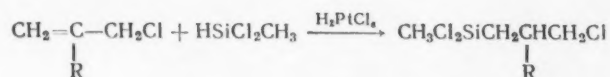
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The synthesis of chloro(3-chloroalkyl)silanes can be effected either by the chlorination of the corresponding alkylchlorosilanes [1-3] or by the addition of silanes containing silicon-attached hydrogen to chloro compounds of the allyl chloride type in presence of a catalyst (platinized charcoal) [4-6]. The latter method appears to be much the simpler, but it requires autoclave conditions at 150-200°. Moreover, the performance of this reaction on a large scale presents considerable danger, because it sometimes proceeds explosively. In the preceding investigation we found [7] that, when the almost homogeneous Speier's catalyst (0.1 N $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol) [8] is used, the addition of dichloromethylsilane to allyl chloride and to 2-methylallyl chloride may be carried out at atmospheric pressure in an ordinary flask:



in which $R = H$ or CH_3 .

In the present work we have made a more detailed investigation of the possibility of synthesizing chloro(3-chloroalkyl)silanes by this method. It was found that, under the conditions which we have described [7], not only dichloromethylsilane, but also diethylmethyl-, chloroethylmethyl-, dichloroethyl-, and trichloro-silanes can be added to allyl and 2-methylallyl chlorides. The rate and exothermic character of the addition of some silanes containing silicon-attached hydrogen to 2-methylallyl chloride are so great that special precautions are necessary in the performance of these reactions. Thus, if a very small amount (about 0.1 ml) of Speier's catalyst is added to a mixture of alkylchlorosilane and 2-methylallyl chloride, after a short induction period (about five minutes) the mixture warms up spontaneously and a violent uncontrollable reaction sets in.

Allyl chloride reacts with silanes containing silicon-attached hydrogen at a much lower rate, so that a mixture of allyl chloride and the silane may be boiled for several hours with Speier's catalyst with gradual rise in the boiling point due to the formation of the chloro(3-chloropropyl)silane. However, the best and safest technique for the performance of such reactions is the following: a small part of the mixture of chloro olefin and silane is heated with Speier's catalyst until either rapid reaction with boiling occurs or the boiling point of the mixture slowly rises above the boiling points of the reactants. The remainder of the mixture must then be added so that its temperature at the boil does not fall below about 100-120°.

The advantages of the method that we have developed lie not only in the simplicity of the apparatus and high yields of chloro(3-chloroalkyl)silanes, but also in the possibility of bringing new silanes and halo olefins into reaction which did not undergo the addition reaction when the previous method [4-6] was used. Thus, even trichlorosilane could not always be caused to add to allyl chloride by the previous method [5, 6], and dichloromethylsilane did not add at all to allyl bromide [5]. Under our conditions both of these reactants underwent addition, though after long boiling.

We also effected the addition of CH_3Cl_2SiH to $CH_2 = C(CH_2Cl)_2$. In Table 1 we give the chloro(3-haloalkyl)silanes obtained by the addition of silanes containing silicon-attached hydrogen to halo compounds of the allyl halide type. These silanes of various structures can be arranged in the following series of diminishing rate of addition to allyl chloride and to 2-methylallyl chloride:

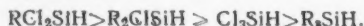


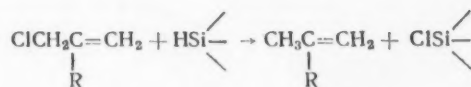
TABLE 1

Reactants				Chloro(2-haloalkyl)silane			B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	M.R.	
chloro olefin	amt. (g)	silane	amt. (g)	formula	amt. (g)	yield (%)				found	calc
$\text{ClCH}_2\text{CH}=\text{CH}_2$	413	HSiCl_3	200	$\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$	110	39	178,4(750)	1,4668	1,3590	43,26	43,27
$\text{ClCH}_2\text{CH}=\text{CH}_2$	306	$\text{HSiCl}_2\text{CH}_3$	460	$\text{CH}_3\text{Cl}_2\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$	326	42	186(760)	1,4585	1,2040	43,45	43,64
$\text{ClCH}_2\text{CH}=\text{CH}_2$	59	$\text{HSiCl}_2\text{C}_2\text{H}_5$	100	$(\text{C}_2\text{H}_5)_2\text{ClSiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$	64	40	205(758)	1,4663	1,1810	48,20	48,15
$\text{ClCH}_2\text{CH}=\text{CH}_2$	76	$\text{HSiClCH}_2\text{C}_2\text{H}_5$	108	$(\text{CH}_3)(\text{C}_2\text{H}_5)_2\text{ClSiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$	79	43	198(758)	1,4548	1,0408	48,28	48,52
$\text{BrCH}_2\text{CH}=\text{CH}_2$	90	$\text{HSiCl}_2\text{CH}_3$	85	$\text{CH}_3\text{Cl}_2\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Br}$	40	22	109(22)	1,4855	1,4690	46,18	46,48
$\text{ClCH}_2\text{C}(\text{CH}_3)=\text{CH}_2$	473	HSiCl_3	260	$\text{Cl}_3\text{Si}(\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl})$	360	81	192,5(740)	1,4685	1,3147	47,83	47,90
$\text{ClCH}_2\text{C}(\text{CH}_3)=\text{CH}_2$	680	$\text{HSiCl}_2\text{CH}_3$	890	$\text{CH}_3\text{Cl}_2\text{Si}(\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl})$	985	63	195(750)	1,4630	1,1710	48,35	48,27
$\text{ClCH}_2\text{C}(\text{CH}_3)=\text{CH}_2$	42	$\text{HSiCl}_2\text{C}_2\text{H}_5$	59	$\text{C}_2\text{H}_5\text{Cl}_2\text{Si}(\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl})$	78	78	215(750)	1,4676	1,1530	52,90	52,78
$\text{ClCH}_2\text{C}(\text{CH}_3)=\text{CH}_2$	29,5	$\text{HSiClCH}_2(\text{C}_2\text{H}_5)$	35,5	$(\text{C}_2\text{H}_5)_2\text{CHSi}(\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl})$	50	77	211(755)	1,4593	1,0202	53,40	53,27
$\text{ClCH}_2\text{C}(\text{CH}_3)=\text{CH}_2$	69	$\text{HSiClCH}_2(\text{C}_2\text{H}_5)_2$	60	$(\text{C}_2\text{H}_5)_2\text{CH}_2\text{Si}(\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl})$	58	45	210(756)	1,4530	0,9002	57,88	58,03
$(\text{ClCH}_2)_2\text{C}=\text{CH}_2$	265	$\text{HSiCl}_2\text{CH}_3$	290	$\text{CH}_3\text{Cl}_2\text{Si}(\text{CH}_2\text{CH}(\text{CH}_2\text{Cl})_2)$	107	20	121,5(18)	1,4870	1,3025	53,01	53,05

TABLE 2

Original chloro(3-chloro-alkyl)silane	Amt. (g)	Time of dehydrochlorination (hr)	Sila-olefin obtained and its yield [% on unrecovered (chloroalkyl)silane]
$\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$	116	40	$\text{Cl}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ (34)
$\text{CH}_3\text{Cl}_2\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$	200	12	$\text{CH}_3\text{Cl}_2\text{SiCH}_2\text{CH}=\text{CH}_2$ (84)
$\text{C}_2\text{H}_5\text{Cl}_2\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$	67	8	$\text{C}_2\text{H}_5\text{Cl}_2\text{SiCH}_2\text{CH}=\text{CH}_2$ (69)
$\text{C}_2\text{H}_5\text{CH}_2\text{ClSiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$	83	4	$\text{CH}_3\text{C}_2\text{H}_5\text{ClSiCH}_2\text{CH}=\text{CH}_2$ (54)
$\text{C}_2\text{H}_5)_2\text{CH}_2\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$	76	18	$(\text{C}_2\text{H}_5)_2\text{CH}_2\text{SiCH}_2\text{CH}=\text{CH}_2$ (14)
$\text{Cl}_3\text{SiCH}_2\text{CHCH}_2\text{Cl}$	272	28	$\text{Cl}_3\text{SiCH}_2\text{C}=\text{CH}_2$ (71)
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{Cl}_2\text{SiCH}_2\text{CHCH}_2\text{Cl} \\ \\ \text{CH}_3 \end{array}$	498	23	$\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_3\text{Cl}_2\text{SiCH}_2\text{C}=\text{CH}_2) \\ \\ \text{CH}_3 \end{array}$ (45)
$\begin{array}{c} \text{C}_2\text{H}_5\text{Cl}_2\text{SiCH}_2\text{CHCH}_2\text{Cl} \\ \\ \text{CH}_3 \end{array}$	84	8	$\begin{array}{c} \text{CH}_3\text{Cl}_2\text{SiCH}=\text{C}(\text{CH}_3)_2 \\ \\ \text{CH}_3 \end{array}$ (20)
			$\begin{array}{c} \text{C}_2\text{H}_5\text{Cl}_2\text{SiCH}_2\text{C}=\text{CH}_2 \\ \\ \text{CH}_3 \end{array}$ (25)
			$\begin{array}{c} \text{C}_2\text{H}_5\text{Cl}_2\text{SiCH}=\text{C}(\text{CH}_3)_2 \\ \\ \text{CH}_3 \end{array}$ (11)

It should be noted that the relative activities of HSiCl_3 and $\text{HSiCl}_2\text{CH}_3$ in their reactions with 2-methylallyl chloride, as determined under competing-reaction conditions, fall in the order given above, whereas a different order has been observed in other cases [13]. The addition of silanes containing silicon-attached hydrogen to 2-methylallyl and allyl chlorides is accompanied, moreover, by the side reaction of the formation of isobutene and of propene, respectively. In the latter case this reaction reduces the yield of chloro(3-chloropropyl)silanes substantially:



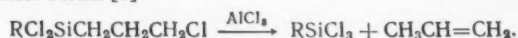
in which $\text{R} = \text{H}$ or CH_3 .

Having a large amount of various chloro(3-chloroalkyl)silanes at our disposal, we investigated various methods for their dehydrochlorination with the object of preparing alkenylchlorosilanes.

It is known [4] that HCl may be split from trichloro(3-chloroalkyl)silanes by boiling them with catalytic amounts of aluminum chloride. Alkenyltrichlorosilanes with the double bond in the α - or β -position are then formed:



However, attempts at the similar dehydrochlorination of chloro(3-chloroalkyl)silanes in which at least one of the three chlorine atoms attached to silicon had been replaced by an alkyl resulted always in the breakdown of the molecule without formation of the sila-olefin [3]

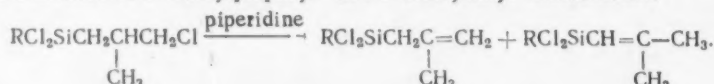


Quinoline was also unable to eliminate hydrogen chloride from these chloro(3-chloroalkyl)silanes, even after long boiling [7].

Searches for methods for the dehydrochlorination of chloro(3-chloroalkyl)silanes led us in the first place to the pyrolytic elimination of HCl [6, 7] and then to dehydrochlorination under the action of piperidine [9, 10]. We have noted previously that some chloro(1-chloroalkyl)- and chloro(2-chloroalkyl)silanes, which are readily dehydrochlorinated by quinoline, will not lose HCl at all under the action of N,N -diethylaniline [9]. It must be supposed that other organic bases may be more effective than quinoline. We therefore, tried out various organic bases on chloro(3-chloroalkyl)silanes, which, as we have mentioned, will not lose HCl at all under the action of quinoline. As a result it was found that piperidine dehydrochlorinates dichloro(3-chloropropyl)methylsilane fairly readily when the reactants were boiled together; it was found that the yields of allyldichloromethylsilane increased with reduction

in the amount of piperidine, i.e., it became clear that there is no need to take piperidine in the amount required for the binding of the whole of the HCl eliminated; it is sufficient to take 5-10% on the weight of chloro(3-chloroalkyl)silane to be dehydrochlorinated. In this case the yields of alkenylchlorosilanes attained maximum values. In this way the chloro(chloroalkyl)silanes listed in Table 2 were dehydrochlorinated. This method for the preparation of allyldichloromethylsilane, dichloromethyl(2-methylallyl)silane, and other alkenylalkyldichlorosilanes is unquestionably the simplest and most convenient method for the synthesis of these compounds.

In the investigation of this method of dehydrochlorination the following regularities were observed. When dehydrochlorinated with piperidine chloro(3-chloro-3-methylpropyl)silanes always [with the exception of $\text{Cl}_3\text{SiCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl}$] formed a mixture of 2-methylpropenyl- and 2-methylallyl-chlorosilanes:



The relative amounts of these two alkenylchlorosilanes varied from experiment to experiment, which suggested the isomerization of (2-methylallyl)silanes into (2-methylpropenyl)silanes during distillation. On the other hand, the dehydrochlorination of chloro(3-chloropropyl)silanes led exclusively to allylchlorosilanes. It was evident that the elimination of HCl occurs most readily from compounds of the alkylidichloro(3-chloroalkyl)silane type.

It was curious that trichloro(2-chloroethyl)silane and dichloro(2-chloroethyl)methylsilane lose HCl under the action of piperidine appreciably less readily than the analogous chloro(3-chloroalkyl)silanes, whereas the relation is the reverse when quinoline is used.

EXPERIMENTAL

Dichloro(3-chloro-2-methylpropyl)ethylsilane $\text{ClCH}_2\underset{\text{CH}_3}{\text{CHCH}_2}\text{SiCl}_2\text{C}_2\text{H}_5$ A part (about 15 ml) of a mixture of

42 g of 2-methylallyl chloride and 59 g of dichloroethylsilane was introduced into a 500-ml flask fitted with reflux condenser, thermometer, and dropping funnel. After the addition of 1 ml of Speier's catalyst [8] and slight warming of the mixture, violent boiling occurred and the boiling point rose to about 120°. Addition of the rest of the mixture was made at such a rate that the boiling point of the contents of the flask did not fall below about 100°. This reaction was strongly exothermic and no heating was necessary. Vacuum distillation gave 80 g (78%) of dichloro(3-chloro-2-methylpropyl)ethylsilane, b.p. 136° (65 mm).

(3-Chloro-2-methylpropyl)diethylmethylsilane $\text{ClCH}_2\underset{\text{CH}_3}{\text{CHCH}_2}\text{Si}(\text{C}_2\text{H}_5)_2\text{CH}_3$ Boiling of a part (about 20 ml) of a

mixture of 69 g of 2-methylallylchloride and 60 g of diethylmethylsilane in presence of 1 ml of Speier's catalyst led to a rise in the boiling point to about 90° only after two hours. The addition of the remainder of the mixture was therefore carried out in large portions. After boiling had continued for 20 hr the boiling point rose to 110°. Distillation through a column gave 30 g (45%) of (3-chloro-2-methylpropyl)diethylmethylsilane, b.p. 210°.

Dichloro[3-chloro-2-(chloromethyl)propyl]methylsilane $(\text{ClCH}_2)_2\text{CHCH}_2\text{SiCl}_2\text{CH}_3$. A mixture of 265 g of $(\text{ClCH}_2)_2\text{C}=\text{CH}_2$, 290 g $\text{CH}_3\text{HSiCl}_2$ and 1 ml of Speier's catalyst was boiled until the boiling point reached 150° (4-5-hr). Vacuum distillation gave 106 g (20%) of $(\text{ClCH}_2)_2\text{CHCH}_2\text{SiCl}_2\text{CH}_3$, b.p. 121.5° (18 mm).

[3-Chloro-2-(chloromethyl)propyl]trimethylsilane $(\text{ClCH}_2)_2\text{CHCH}_2\text{Si}(\text{CH}_3)_3$. To CH_3MgCl prepared from 25 g of magnesium in 500 ml of ether we added 106 g of $(\text{ClCH}_2)_2\text{CHCH}_2\text{SiCl}_2\text{CH}_3$. The contents of the flask were then boiled for three hours and decomposed with water. The ether layer and ether extracts of the water layer were dried with calcium chloride. Fractionation through a column gave 42 g (32%) of $(\text{ClCH}_2)_2\text{CHCH}_2\text{Si}(\text{CH}_3)_3$; b.p. 98-100° (25 mm); n_D^{20} 1.4638, d_4^{20} 1.0241; found MR 53.66; calculated MR 53.85. The addition of the other silanes to 2-alkenyl chlorides (see Table 1) was carried out under analogous conditions. Some of the experiments were described in previous papers [7, 10].

Allyldichloromethylsilane $\text{CH}_2=\text{CHCH}_2\text{SiCl}_2\text{CH}_3$. A mixture of 191 g of dichloro(3-chloropropyl)methylsilane and 9 g of piperidine was prepared in a 250 ml flask fitted with a long (300 mm) Vigreux column. The contents of the flask were distilled slowly at such a rate that the temperature of the outgoing vapor was not above 120-130°, for which 12 hours was necessary. Distillation of the condensate through a column gave 16 g of trichloromethylsilane, b.p. 65-66°, 112 g of allyldichloromethylsilane, b.p. 117-118°, and 20 g of unchanged dichloro(3-chloropropyl)methylsilane, b.p. 184-185°. The yield of allyldichloromethylsilane was 72%, or 84% on the unrecovered dichloro(3-chloropropyl)methylsilane.

TABLE 3

Sila-olefin	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR	
				found	calc. [12]
$\text{Cl}_2\text{SiCH}_2\text{CH}=\text{CH}_2$	116 (750)	1,4445	1,2224	38,18	38,14
$\text{Cl}_2\text{CH}_2\text{SiCH}_2\text{CH}=\text{CH}_2$	117,5 (747)	1,4406	1,0686	38,30	38,51
$\text{Cl}_2\text{C}_2\text{H}_5\text{SiCH}_2\text{CH}=\text{CH}_2$	143,5 (745)	1,4483	1,0529	43,00	42,96
$\text{CH}_3(\text{C}_2\text{H}_5)_2\text{SiCH}_2\text{CH}=\text{CH}_2$	135,8 (760)	1,4380	0,9109	42,86	43,39
$(\text{C}_2\text{H}_5)_2\text{CH}_2\text{SiCH}_2\text{CH}=\text{CH}_2$	142 (755)	1,4342	0,7727	47,84	48,27
$\text{Cl}_3\text{SiCH}_2-\text{C}=\text{CH}_2$	139,5 (762)	1,4535	1,2036	42,61	42,64
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{Cl}_2\text{SiCH}_2\text{C}=\text{CH}_2 \end{array}$	139 (747)	1,4470	1,0521	42,95	42,96
$\begin{array}{c} \text{CH}_3 \\ \\ \text{C}_2\text{H}_5\text{Cl}_2\text{SiCH}_2\text{C}=\text{CH}_2 \end{array}$	164,5 (747)	1,4570	1,0549	47,50	47,59
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{Cl}_2\text{SiCH}=\text{C}(\text{CH}_3)_2 \end{array}$	149 (747)	1,4558	1,0476	43,83	43,41
$\text{C}_2\text{H}_5\text{Cl}_2\text{SiCH}=\text{C}(\text{CH}_3)_2$	170,5 (745)	1,4620	1,0508	48,18	48,04

$\text{CH}_2=\text{CCH}_2\text{SiCH}_2\text{Cl}_2$
Dichloromethyl(2-methylallyl)silane
CH₃
and dichloromethyl(2-methylpropenyl)silane

$(\text{CH}_3)_2\text{C}=\text{CH}_2\text{SiCH}_2\text{Cl}_2$. A mixture of 489 g of dichloro(3-chloro-2-methylpropyl)methylsilane and 25 g of piperidine was distilled from a 500-ml flask at such a rate that the temperature of the outgoing vapor was not above 155° (18 hr was required). Distillation of the condensate through a column gave 38 g of trichloromethylsilane and 50 g of unchanged dichloro(3-chloro-2-methylpropyl)methylsilane. We then isolated 184 g of dichloromethyl(2-methylallyl)silane, b.p. 138-139°, and 81.5 g of dichloromethyl(2-methylpropenyl)silane, b.p. 149-150°. The total yield of alkenyldichloromethylsilanes was 65%, or 72% on the amount of dichloro(3-chloro-2-methylpropyl)methylsilane that reacted.

Allyltrichlorosilane $\text{CH}_2=\text{CHCH}_2\text{SiCl}_3$. Boiling of 110 g of trichloro(3-chloropropyl)silane with 5 g of piperidine for 20 hr was not accompanied by dehydrochlorination, but then slow elimination of HCl began (the temperature of the outgoing vapor could not be kept above 140°). By distillation of the condensate we isolated 16 g of allyltrichlorosilane and 53 g of unchanged trichloro(3-chloropropyl)silane. The yield of allyltrichlorosilane was 18%, or 34% on the unrecovered $\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$.

In an analogous way the chloro(3-chloroalkyl)silanes listed in Table 2 were dehydrochlorinated. It should be noted that, for some unexplained reason, the elimination of HCl sometimes did not begin until after 10-20 hr of boiling, though in other experiments on the same chloro(3-chloroalkyl)silanes dehydrochlorination set in smoothly after the first minutes of boiling.

The residues left in the stills after the dehydrochlorination experiments underwent elimination of HCl particularly vigorously without any period of induction. The properties of the sila-olefins obtained are given in Table 3. Some of the experiments on dehydrochlorination with the aid of piperidine have been described previously [10, 11].

SUMMARY

1. A method was developed for the synthesis of unsaturated organosilicon compounds by the dehydrochlorination of various chloro(3-chloroalkyl)silanes with catalytic amounts of piperidine.

2. A method not requiring the use of an autoclave was developed for the synthesis of chloro(3-chloroalkyl)silanes by the addition of various silanes containing silicon-attached hydrogen to 2-alkenyl chlorides in presence of H_2PtCl_6 .

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NEW METHOD FOR THE PREPARATION OF
OF ORGANOSILICON MONOMERS
BY THE HIGH-TEMPERATURE CONDENSATION
OF ALKENYL CHLORIDES, ARYL CHLORIDES, AND OLEFINS
WITH SILANES CONTAINING SILICON-ATTACHED HYDROGEN

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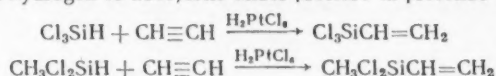
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

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For the preparation of some organosilicon polymers, monomers such as trichlorovinylsilane, dichloromethylvinylsilane, trichlorophenylsilane, and dichloromethylphenylsilane are required. However, whereas industrial methods exist for the synthesis of chlorophenylsilanes, no economically satisfactory methods have yet been developed for the preparation of chlorovinylsilanes. The direct method of synthesis, which has been successfully used in the preparation of methyl-, ethyl-, and phenyl-chlorosilanes has been found to be quite inapplicable for the case of chlorovinylsilanes because the yield of desired products does not exceed a few percent [1]. Only the method of chlorinating chloroethylsilanes and subsequent dehydrochlorination of the chloro(chloroethyl)silanes afforded the possibility of synthesizing chlorovinylsilanes in appreciable yield (about 30%), through this is a multistage method [2].

In the Hydrocarbon Chemistry Laboratory of the Institute of Organic Chemistry of the Academy of Sciences a method has recently been developed for the synthesis of chlorovinylsilanes by the addition of the corresponding silanes containing silicon-attached hydrogen to acetylene under pressure in presence of chloroplatinic acid as catalyst [3].



However, this method is associated with some difficulties in its practical use since it demands the setting up of apparatus for work with acetylene under pressure and a certain consumption of expensive catalyst. Simultaneously, therefore, we have developed a method of noncatalytic high-temperature condensation of alkenyl and aryl chlorides with silanes containing silicon-attached hydrogen.

The starting point for our investigation was Agry's observation [4] of the reaction between trichlorosilane and trichloroethylene on passage of the mixture through an empty quartz tube at 600°, when trichloro(2,2-dichlorovinyl)silane and hydrogen chloride are formed:*



In a later investigation Agry [6] found that 1,2-dichloroethylenes also react analogously with trichlorosilane, whereas vinylidene dichloride does not undergo the analogous reaction:



*For a long time the structure of the compound obtained by Agry remained in doubt, for Agry himself first considered that it had the structure of trichloro(1,2-dichlorovinyl)silane, but later, after Wagner and Pines [5] had raised objections to this, he agreed [6] with the latter that the compound was trichloro(2,2-dichlorovinyl)silane. However, subsequently on the basis of spectral and electron-diffraction methods of investigation, Murata [7] maintained that this substance was nevertheless trichloro(1,2-dichlorovinyl)silane. We synthesized both trichloro(1,2-dichlorovinyl)- and trichloro(2,2-dichlorovinyl)-silanes, and by spectrum analysis we finally established that trichloro(2,2-dichlorovinyl)silane is formed in Agry's reaction and that Murata's views were erroneous.

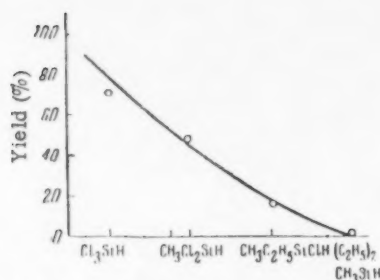


Fig. 1. Relation of yield of chlorovinylsilane to structure of hydride silane.

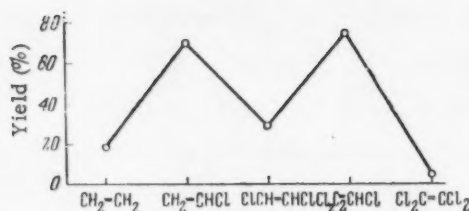
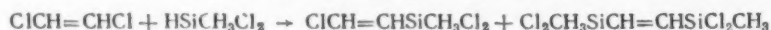


Fig. 2. Yields of alkenylchlorosilanes in the condensation of HSiCl₃ with ethylene and chloroethylenes.

However, these interesting observations were not followed up by Agry or by other investigators until quite recently.

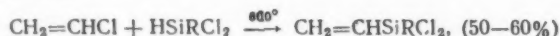
Moreover, the reactions observed by Agry were not postulated by anybody as a new method for the formation of the Si-C bond. In Eaborn's recent monograph [9], as in other reviews, these reactions are assigned to the section on the addition of silanes containing silicon-attached hydrogen to unsaturated compounds.

In a desire to verify the generality of high-temperature condensation, i.e., to determine whether Agry's observation forms a special case of a general reaction between silanes containing silicon-attached hydrogen ("hydride silanes") and chloro olefins, in 1956 we undertook an investigation in this direction [8, 10-17]. In the first place we convinced ourselves [10] that trichloroethylene and 1,2-dichloroethylene react readily with more complicated "hydride silanes," namely methyl- and ethyl-dichlorosilanes, which widened substantially the possibilities of synthesis by high-temperature condensation and led to the preparation of carbofunctional organosilicon monomers suitable for the preparation of linear polysiloxanes:



In the last case we isolated not only dichloro(2-chlorovinyl)methylsilane, but also 1,2-bis(dichloromethylsilyl)ethylene. It was shown also that the yields of condensation products were almost independent of whether cis- or trans-dichloroethylene was used in the reaction.

Having successfully carried out the above reactions and convinced ourselves that not only HSiCl₃, but also R₂HSiCl₂ may be used, we then investigated the use of other chloro olefins in high-temperature condensation with these hydride silanes. As an alkenyl chloride we used vinyl chloride and obtained high yields of trichlorovinylsilane and alkylchlorovinylsilanes [11-13]:



in which R = Cl, CH₃, and C₂H₅.

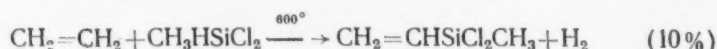
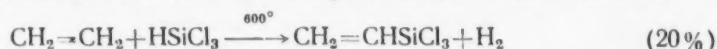
More detailed investigation showed that the optimum reaction temperature was 580-590° with a contact time of 20-25 sec. Moreover, it was found that this reaction may be carried out also in an empty iron tube, which was convenient for the performance of the reaction in practice. Thus, the simplicity of the apparatus required, the availability of the reactants, the safety of the process, and the high yields obtained make this method of synthesis of chlorovinylsilanes the most convenient of all at present available [direct synthesis, addition of hydride silanes to acetylene, the dehydrochlorination of chloro(chloroethyl)silanes].

Extending this method to the synthesis of chlorovinylsilanes, we investigated [14] the high-temperature condensation of vinyl chloride with all hydride silanes of the series HSiR_nCl_{3-n}, in which n = 0, 1, 2, and 3. It was found that the best yields (up to 80%) were given by trichlorosilane (n = 0), but trialkylsilanes (n = 3) do not undergo condensation at all with formation of chlorovinylsilanes (Fig. 1). Another reaction occurs, and this we refer to as reduction, rather than condensation:



A similar reaction occurs also with other hydride silanes, but the contribution made by this reaction diminishes sharply as we pass from R_3SiH to Cl_3SiH .

We considered it to be of interest also to investigate ethylene and the whole series of chloroethylenes up to tetrachloroethylene under the conditions for high-temperature condensation [14]. Tetrachloroethylene condenses with trichlorosilane, but with the lowest yields obtained throughout the whole series investigated [trichloro(trichlorovinyl)silane was formed in the yield of only about 5%].* The reaction with ethylene [12] went with formation of a mixture of ethyl- and vinyl-chlorosilanes, in which the latter predominated (70-80%) [12, 14, 15].



The yields of condensation products in the series of chloroethylenes investigated followed the relation shown in Fig. 2 as we passed from ethylene to tetrachloroethylene.

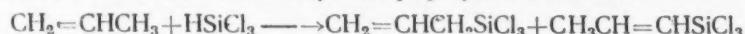
Before our investigation it was known only that hydride silanes can react with ethylene with formation of alkyl-chlorosilanes by the radical-addition mechanism [19].



or by the mechanism of radical telomerization [20]



Therefore, wishing to verify the generality of the newly discovered reaction of hydride silanes with ethylene, we studied the reaction between trichlorosilane and propene under analogous conditions [14, 15]. A fraction was isolated in low yield (10%) which consisted of a mixture of allyl- and propenyl-trichlorosilanes;



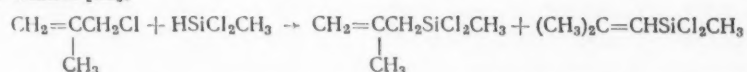
Hence, this third way, discovered by us, in which hydride silanes can react with olefins (ethylene and propene) is a new reaction in the organic chemistry of silicon. We consider that this reaction also has a free-radical mechanism. To extend the scope of the method further, we decided to investigate chloro olefins of the allyl chloride type, in particular allyl and 2-methylallyl chlorides, in the high-temperature condensation reaction. It was found that reaction of dichloromethylsilane and of trichlorosilane with allyl chloride gave good yields (30-40%) of the corresponding allylchlorosilanes [12, 13, 16]:



in which $R = CH_3$ and H .

In this reaction there usually result also very small amounts of chloropropenylsilanes, which increase greatly in amount when the process is carried out in an iron tube.

2-Methylallyl chloride also undergoes the high-temperature condensation with formation of 2-methylallyl- and 2-methylpropenyl-silanes [12]:



It is interesting to note that in the liquid-phase free-radical reaction of allyl, 2-methylallyl, and vinyl chlorides, and also of ethylene and propene, with hydride silanes the latter add at the double bond of the unsaturated compound, but in the gas phase (the conditions of the high-temperature condensation studied by us) there occurs the replacement of a chlorine or hydrogen atom (in ethylene and propene) by a silyl group with preservation of the double bond. The chloro olefins which give high yields in the addition reaction give low yields in the high-temperature condensation, and vice versa. Hence, on the basis of the above discussion we may conclude that the high-temperature

*McBee, Roberts, and Puerckhauer [18] made a detailed investigation of the condensation of tetrachloroethylene with hydride silanes simultaneously with us. They obtained a 14% yield of trichloro(trichlorovinyl)silane with an olefin : trichlorosilane ratio of 2 : 1. We used a ratio of 1 : 1.

TABLE 1

Reactants		Compounds obtained (yields in %)
hydride silane	olefin or chloro olefin	
Cl ₃ SiH	CH ₂ =CH ₂	Cl ₃ SiCH=CH ₂ (17%); Cl ₃ SiC ₂ H ₅ (4%)
Cl ₂ CH ₂ SiH	CH ₂ =CH ₂	Cl ₂ CH ₂ SiCH=CH ₂ (12%); Cl ₂ CH ₂ SiC ₂ H ₅ (3%)
Cl ₃ SiH	CH ₂ =CH-CH ₃	CH ₂ =CHCH ₂ SiCl ₃ (5%); CH ₃ CH=CHSiCl ₃ (5%)
Cl ₃ SiH	ClCH=CH ₂	Cl ₃ SiCH=CH ₂ (60%)
CH ₃ Cl ₂ SiH	ClCH=CH ₂	CH ₃ Cl ₂ SiCH=CH ₂ (52%)
C ₂ H ₅ Cl ₂ SiH	ClCH=CH ₂	C ₂ H ₅ Cl ₂ SiCH=CH ₂ (27%)
C ₂ H ₅ CH ₂ ClSiH	ClCH=CH ₂	C ₂ H ₅ CH ₂ ClSiCH=CH ₂ (15%)
CH ₃ Cl ₂ SiH	ClCH=CHCl	CH ₃ Cl ₂ SiCH=CHCl (20%); Cl ₂ CH ₂ SiCH=CHSiCl ₂ CH ₃ (18%)
Cl ₃ SiH	ClCH=CCl ₂	Cl ₃ SiCH=CCl ₂ (65%)
CH ₃ Cl ₂ SiH	ClCH=CCl ₂	CH ₃ Cl ₂ SiCH=CCl ₂ (28%)
C ₂ H ₅ Cl ₂ SiH	ClCH=CCl ₂	C ₂ H ₅ Cl ₂ SiCH=CCl ₂ (12%)
Cl ₃ SiH	Cl ₂ C=CCl ₂	Cl ₃ SiCCl=CCl ₂ (5%)
Cl ₃ SiH	ClCH ₂ CH=CH ₂	Cl ₃ SiCH ₂ CH=CH ₂ (40%)
CH ₃ Cl ₂ SiH	ClCH ₂ CH=CH ₂	CH ₃ Cl ₂ SiCH ₂ CH=CH ₂ (30%); CH ₃ Cl ₂ SiCH=CHCH ₃ (5%)
CH ₃ Cl ₂ SiH	ClCH ₂ C=CH ₂	Cl ₂ CH ₂ SiCH ₂ C=CH ₂ (15%); CH ₃ Cl ₂ SiCH=C(CH ₃) ₂ (7%)
CH ₃ Cl ₂ SiH	$\begin{array}{c} \text{CH}_3 \\ \\ \text{ClCH}=\text{C}(\text{CH}_3)_2 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{Cl}_2\text{CH}_2\text{SiCH}_2\text{C}=\text{CH}_2 \text{ (8\%); } \text{CH}_3\text{Cl}_2\text{SiCH}=\text{C}(\text{CH}_3)_2 \text{ (15\%)} \end{array}$
Cl ₃ SiH	CH ₂ =CCl ₂	Cl ₃ SiCCl=CH ₂ (3%); Cl ₃ SiCH=CH ₂ (16%)
CH ₃ Cl ₂ SiH	ClCH ₂ CH ₂ Cl	CH ₃ Cl ₂ SiCH=CH ₂ (10%)
Cl ₃ SiSiCl ₃	CH ₂ =CHCl	CH ₃ =CHSiCl ₃ (20%); SiCl ₄ (40%)

condensation of hydride chlorosilanes (HSiCl₃, RSiCl₂H) with mono- and poly-chloro olefins form a new general and convenient method for the synthesis of unsaturated organosilicon monomers (Table 1).

This reaction is essentially a fundamentally new method of forming an Si-C bond and can be called homolytic silylation. The use of various aryl chlorides under high-temperature condensation conditions also gave interesting results.

Before our investigation the following three methods for the synthesis of aromatic organosilicon monomers had found practical application: a) organometallic (Grignard) synthesis [21]; b) direct reaction of aryl chlorides with silicon-copper [21, 22]; c) reaction of hydride silanes with aromatic compounds under pressure at high temperature, i.e., in the liquid phase according to the scheme [23-28]:



Each of these methods has substantial disadvantages. The performance of the Grignard reaction on the large scale in industry encounters great difficulties because of the necessity of separating the reaction products from the large amount of magnesium halide formed.

The direct method of synthesis does not give high yields of chlorophenylsilanes and it is at present impossible to obtain monomers with different groups on the silicon, e.g. dichloromethylphenylsilane, by this method. The third method requires high-pressure apparatus. We propose a fourth method for the synthesis of aromatic organosilicon monomers by the reaction of hydride silanes with aryl chlorides at a high temperature (550-700°), but atmospheric pressure, i.e., in the gas phase (condensation reaction):



in which R = aryl; R' = CH₃ or C₂H₅; n = 0, 1. Some of the results of this work have been published [13, 29-33], and here we give a generalization of the results.

TABLE 2

Reactants		Compounds obtained (yield in %)
hydride silane	aryl chloride	
HSiCl ₃	C ₆ H ₅ Cl	C ₆ H ₅ SiCl ₃ (52%) **
HSiCl ₃	<i>p</i> -CH ₃ C ₆ H ₄ Cl	<i>p</i> -CH ₃ C ₆ H ₄ SiCl ₃ (55%)
HSiCl ₃	<i>o</i> -CH ₃ C ₆ H ₄ Cl	<i>o</i> -CH ₃ C ₆ H ₄ SiCl ₃ (45%)
HSiCl ₃	<i>p</i> -ClC ₆ H ₄ Cl	<i>p</i> -ClC ₆ H ₄ SiCl ₃ (29%); <i>p</i> -Cl ₃ Si·C ₆ H ₄ SiCl ₃ (15%)
HSiCl ₃	2,3-(CH ₃) ₂ C ₆ H ₃ Cl	2,5-(CH ₃) ₂ C ₆ H ₃ SiCl ₃ (50%)
HSiCl ₃	2,4,6-(CH ₃) ₃ C ₆ H ₂ Cl	2,4,6-(CH ₃) ₃ C ₆ H ₂ SiCl ₃ (50%)
HSiCl ₃	α -C ₁₀ H ₇ Cl	α -C ₁₀ H ₇ SiCl ₃ (60%) **
HSiCl ₃	β -C ₁₀ H ₇ Cl	β -C ₁₀ H ₇ SiCl ₃ (48%)
HSiCl ₃	C ₆ H ₅ CH=CH ₂ Cl	C ₆ H ₅ CH=CH ₂ SiCl ₃ (75%)
HSiCl ₃	<i>p</i> -CH ₂ =CHC ₆ H ₄ Cl	<i>p</i> -CH ₂ =CHC ₆ H ₄ SiCl ₃ (25%)
CH ₃ SiHCl ₂	C ₆ H ₅ Cl	C ₆ H ₅ —SiCl ₂ CH ₃ (35%)
CH ₃ SiHCl ₂	<i>p</i> -ClC ₆ H ₄ Cl	<i>p</i> -ClC ₆ H ₄ SiCl ₂ CH ₃ (20%); <i>p</i> -(CH ₃ Cl ₂ Si)C ₆ H ₄ SiCl ₂ CH ₃ (8%)
CH ₃ SiHCl ₂	α -C ₁₀ H ₇ Cl	α -C ₁₀ H ₇ SiCl ₂ CH ₃ (49%)
CH ₃ SiHCl ₂	β -C ₁₀ H ₇ Cl	β -C ₁₀ H ₇ SiCl ₂ CH ₃ (40%)
C ₂ H ₅ SiHCl ₂	α -C ₁₀ H ₇ Cl	α -C ₁₀ H ₇ SiCl ₂ C ₂ H ₅ (19%)
C ₆ H ₅ SiHCl ₂	C ₆ H ₅ Cl	(C ₆ H ₅) ₂ SiCl ₂ (35%)

*The yields are given on the original hydride silane.

**Under the conditions of the direct synthesis the yields of C₆H₅SiCl₃ and C₁₀H₇SiCl₃ did not exceed 25% [22, 37].

Before our investigation there had appeared two patents [34, 35] on reactions of this type, and in both of these it was stated that to carry out the reaction a catalyst (copper or palladium) needed to be present. We showed that, when the reaction is carried out at 550–700°, aryl chlorides condense quite satisfactorily with hydride silanes without any catalyst with formation of arylchlorosilanes. The reaction was carried out in an empty quartz tube heated in a tube furnace or in any other way by the passage of a mixture of the aryl chloride and the hydride silane at rates of feed ensuring a contact time of 10–100 sec. In this way the process could be carried out continuously. The relative extents of the condensation and reduction reactions depend substantially on the material of the tube. Thus, whereas under given conditions at 600° the yields of trichlorophenylsilane and dichloromethylphenylsilane in reactions in a quartz tube were 52% and 35%, respectively, the corresponding yields obtained with a ceramic tube were 46% and 26%, and those in a tube of 1Kh18N9T stainless steel were only 28% and 10%. As hydride silanes we used trichlorosilane, dichloromethylsilane, and dichloroethylsilane, and as aryl chlorides we used chlorobenzene, *p*-dichlorobenzene, 1- and 2-chloronaphthalenes, and various alkyl derivatives of chlorobenzene. In all cases the condensation products were obtained in quite satisfactory yields. The yields of some of the arylchlorosilanes obtained in this way are given in Table 2.

Hence, this method is general for the preparation of any chloroarylsilane having three or two atoms of chlorine attached to silicon. Recently the generality of the method has been extended by the use of dichlorosilane, instead of a monohydride silane; this permits the synthesis of alkenyl- and aryl-dichlorosilanes (RHSiCl₂ [36]). It must be supposed that under the conditions of high-temperature condensation silicon compounds may also be used which have three atoms of directly attached hydrogen, and also silane (SiH₄).

As will be seen from Table 2, the yields of monomers in the high-temperature condensation are about the same as in the catalytic reaction of aromatic compounds with hydride silanes—sometimes higher.

By variation of the contact time for each given reaction temperature quantitative reaction of the hydride silane can always be assured. It is interesting that the maximum yields of arylchlorosilanes obtained at various temperatures with various contact times are approximately the same. It was therefore found possible to construct a graph showing the relation between contact time and reaction temperature for the obtaining of maximum yield of arylchlorosilane. For trichlorophenylsilane (maximum yield 50%) this relation is shown in Fig. 3.

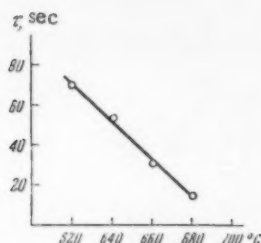
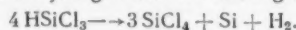


Fig. 3. Relation between time of contact and reaction temperature in the preparation of trichlorophenylsilane in maximum yield (about 50%).

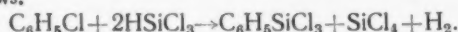
Together with the main reaction, which gives the arylchlorosilane, the aryl chloride and hydride silane react as follows (reduction reaction):



In the case of chlorobenzene up to 30% of the hydride silane is consumed in this side reaction, but in the case of chloronaphthalene this reaction occurs to a smaller extent. In addition, to a slight extent there occurs the pyrolysis of the hydride silane with liberation of hydrogen and silicon, e.g., for $HSiCl_3$:



The gas-phase reaction of hydride silanes with aryl chlorides at atmospheric pressure proceeds with a quite different mechanism from the liquid-phase reaction of the same reactants. In the case of the noncatalytic liquid-phase reaction, the main reaction products are arylchlorosilane, silicon tetrachloride, and hydrogen, and hydrogen chloride is not liberated. According to the views of Barry, Gilkey, and Hook [28] the reaction proceeds by the mechanism of electrophilic substitution. The scheme of reaction, e.g., of chlorobenzene with trichlorosilane, can be represented as follows:



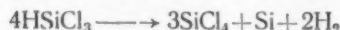
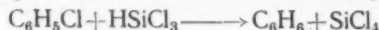
The main products of the catalytic liquid-phase reaction of aryl chloride with a hydride silane are a chloro(chloro-aryl)silane and hydrogen chloride:



The main products of the gas phase reaction of aryl chlorides with hydride silane are arylchlorosilanes and hydrogen chloride.



As by-products an aromatic hydrocarbon, silicon tetrachloride, and hydrogen are formed:

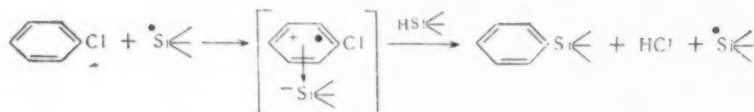


The occurrence of the gas-phase reaction of hydride silanes with aryl chlorides only at high temperature and also its occurrence with the greatest success in an empty tube, i.e., when the surface of the walls is at a minimum, prompts the suggestion that the given reaction has a free-radical character. It is well known that at high temperatures hydride silanes readily break down into the radicals $H\cdot$ and $Si\cdot$.

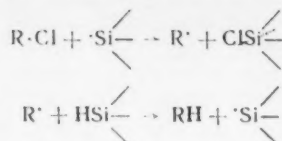
By a detailed investigation of the mechanism of the reaction of organic chloro compounds with hydride silanes it was shown that condensation (1) and reduction (2) are parallel reactions:



In both cases the active initiator is the silyl radical $Si\cdot$. In the condensation the silyl radical forms π -complex in the intermediate stage with the aid of the π -electrons of the aromatic ring or the double bond, and this, breaking down on collision with a hydride silane molecule, gives the condensation product, e.g:

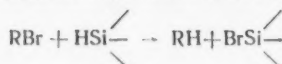


In the reduction the attack of the silyl radical is directed directly at the chlorine atom of the aryl or alkenyl chloride:



It will be seen that in both cases the silyl radical is regenerated, and it serves for the propagation of the chain.

Thus, the high-temperature reactions of hydride silanes with aryl and alkenyl chlorides constitute a new form of free-radical interaction between hydride silanes and these compounds. It is interesting that the use of aryl or alkenyl bromides in the reaction leads to its almost quantitative occurrence in accordance with the reduction scheme:



This reaction begins to predominate as we pass gradually from trichlorosilane to trialkylsilanes.

In view of the above discussion it would be expected that $\text{Cl}_3\text{SiSiCl}_3$, which breaks down to silyl radicals at high temperatures, would react with, in particular, vinyl chloride by an analogous scheme. In fact on the simultaneous passage of vinyl chloride and hexachlorodisilane through a quartz tube heated to 600° trichlorovinylsilane is formed [14, 17]:



EXPERIMENTAL

High-temperature condensation of ethylene with trichlorosilane. Ethylene was passed at a rate of 15 liters/hr through an empty glass tube (length 1000 mm, diameter 15 mm) heated to 600° . From a dropping funnel 485 g of trichlorosilane was introduced into the tube at a rate of one drop per second. Distillation of the condensate through a column gave 185 g of unchanged Cl_3SiH , 50 ml of SiCl_4 , and 80 g of a fraction of b.p. $90-98^\circ$. Redistillation of this fraction through a column gave 40 g of pure (according to the Raman spectrum) trichlorovinylsilane, b.p. $92-93^\circ$, and 35 g of a fraction of b.p. $93-98^\circ$, which, on the basis of the Raman spectrum, was found to consist of 50% of trichloroethylsilane and about 50% of trichlorovinylsilane. Hence, the yield of trichlorovinylsilane was 17% on the trichlorosilane that reacted.

Also, 100 g of a nondistilling viscous liquid, which fumed in air, remained in the flask after the distillation. The amount of this which was probably polymerized ethylene, increases considerably when the reaction is carried out at 700° . Under analogous conditions, propene forms a similar polymer.

All the remaining reactions were carried out under analogous conditions when one component was a gas. When both components were liquids, the general procedure in the synthesis did not differ from that described above. In most cases the condensation temperature was 600° (see Table 1).

Synthesis of trichlorophenylsilane. The reaction was carried out in an empty quartz tube with a diameter of 8 mm and a length of the working (heated) part of 1800 mm. The temperature in the reaction zone was measured with a thermocouple, which was inserted in the tube. The doser (a Balandin buret or an automatic spray buret) contained a mixture of chlorobenzene (225 g; 2 moles) and trichlorosilane (135.5 g; 1 mole). The mixture was fed into the tube at a rate of 45 g/hr (which corresponds to a contact time of 15 sec) with a temperature of the reaction zone of 680° . On leaving the reaction tube the vapor passed to a Liebig condenser, where it was condensed and collected in a receiver. To trap residues of uncondensed trichlorosilane a trap, cooled with acetone and solid carbon dioxide, was placed beyond the receiver. The amount of condensate collected was 330 g. Fractionation through a column of 40-plate efficiency gave the following products: trichlorosilane (b.p. $31-33^\circ$), 1.5 g; silicon tetrachloride (b.p. $55-57^\circ$), 47.6 g; benzene (b.p. $78-80^\circ$), 15.8 g; chlorobenzene (b.p. $129-132^\circ$), 118.7 g; trichlorophenylsilane (b.p. $198-201^\circ$), 110.5 g; residue, 6.3 g.

Hence, calculated on the amount of trichlorosilane taken, the yield of trichlorophenylsilane was 52%. The remaining syntheses differed only in the temperature of the reaction zone and the contact time and are not described here.

SUMMARY

1. The high-temperature condensation (600-700°) of alkenyl and aryl chlorides with hydride silanes (i.e., silanes containing silicon-attached hydrogen) in a flow system at atmospheric pressure is a general method for the synthesis of alkenyl- and aryl-chlorosilanes. On the basis of this new method we developed syntheses, differing from those known previously in their simplicity and high yields, for various organosilicon monomers.
2. A reaction scheme is proposed for the high-temperature condensation of hydride silanes with alkenyl and aryl chlorides; the scheme requires the participation of free radicals.
3. A new reaction of hydride silanes with olefins leading to the formation of alkenylchlorosilanes was discovered.

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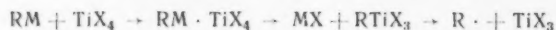
All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

REACTIONS OF ORGANOMETALLIC COMPOUNDS
WITH HEAVY-METAL SALTS
COMMUNICATION 4. REACTION OF ETHYLLITHIUM
WITH TITANIUM TRICHLORIDE

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Data in the literature on the reaction of organometallic compounds with titanium salts refer mainly to the reactions of organoaluminum [1, 2], organomagnesium, and organolithium [2-4] compounds with quadrivalent titanium derivatives (halides and alkoxy derivatives). According to the generally accepted scheme of the reaction proposed by Gilman [4], the process includes several stages, in each of which the reduction of a titanium salt occurs:



It is further supposed that the process may proceed in a similar way up to the formation of TiX_2 and metallic titanium. Similar conclusions were reached by Friedlander and Oita [2], who studied the reaction between ethyllithium and titanium tetrachloride.

As one of the proofs of the presence of a free-radical stage some investigators accept the ability of the reaction system to initiate the polymerization of olefins and dienes [2, 4, 5]. In a previous paper [6] we gave the results of some experiments on the reaction of ethyllithium with titanium tetrachloride. In the present investigation we studied the reaction of ethyllithium with the crystalline violet α -modification of titanium trichloride in hydrocarbon media. Reaction between these compounds starts at even a fairly low temperature (-40°) and is accompanied by change in the color of the precipitate from violet to green. The appearance of a green color in the solution indicates the formation of new soluble organometallic compounds or their complexes. With rise in temperature the color changes to brown and then further to black (formation of reduced forms of titanium). The mixing of a solution of ethyllithium with a suspension of titanium trichloride at room temperature leads to a highly exothermic reaction with the liberation of gaseous products.

The formation of green precipitates in the reaction of titanium chlorides with organoaluminum compounds is generally associated with the appearance of organotitanium compounds [7, 8] containing tervalent titanium. The preliminary experiments that we carried out showed that the precipitates formed contained organometallic compounds which were not removed when the reaction product was washed with organic solvents. On decomposition of the washed precipitate with water or alcohol the corresponding amounts of ethane were liberated, which could be associated with the presence either of alkylalotitaniums or of an insoluble complex of titanium halide with ethyllithium.

We studied the reaction at 0° , 20° , 55° , and 100° with various molar proportions of ethyllithium and titanium trichloride. An ampoule was first heated at 250° in a vacuum and filled with nitrogen or argon; a solution of ethyllithium in octane or nonane was then poured into the ampoule, which was placed in a thermostat and agitated while ground titanium trichloride was added. In some experiments the order of the addition of the reactants was reversed: the ethyllithium solution was added to a suspension of titanium trichloride in the hydrocarbon. The gases liberated in the reaction were collected in a gas holder or buret; the reaction mixture was kept at the required temperature for 2-26 hr, and the apparatus was then purged with dry nitrogen or argon, and all gases were collected in the same gas holder. In some experiments the ampoule was centrifuged and the solution was separated by decantation; solvent was added, and the mixture was again centrifuged; the amount of ethyllithium remaining in the solution was determined from the amount of ethane liberated on decomposition of the solution with water. A separate

TABLE 1. Yield of Reaction Gases and Their Composition

Expt	Molar ratio LiC_2H_5 per TiCl_3	Temp. (°C)	Yield (%)	Composition of gas mixture (%)		
				ethane	ethylene	butane
1	0,63	0	22	62	19	19
2	1,35	0	14	55	27	18
3	1,36	55	60	65	19	16
4	1,78	100	81	60	25	15
5	2,12	0	8	68	20	12
6	1,95	55	49	61	27	12
7	1,82	100	80	53	30	17
8	1,96	100	72	42	50	8
9	3,5	55	73	35	49	16
10	6,15	100	89	31	64	5
11	6,97	100	100	38	53	9

TABLE 2. Composition of the Gaseous Products of the Decomposition of Ethyllithium in Nonane at 100°

Substance	Reaction time (hr)	Composition of gas (%)			Yield of hydrocarbons (%) on LiC_2H_5 taken for reaction
		ethane	ethylene	butane	
LiC_2H_5	14	15	70	15	25
$\text{LiC}_2\text{H}_5 + \text{TiCl}_3$	Very short	31	64	5	89

determination was made of the amount and composition of the gas liberated on decomposition of the washed precipitate.

It will be seen from Table 1 that the ratio of the amounts of the reactants affects the composition of the reaction gas more than the reaction temperature does. With equimolecular proportions, and even with proportions close to 2 : 1, ethane predominates in the reaction gas, amounting on the average to 56%; with a ratio of greater than 2 : 1, there is an appreciable increase in the amount of ethylene. In experiments with a considerable excess of ethyllithium (6 : 1; 7 : 1) the amount of ethylene in the gas exceeds the amount of ethane.

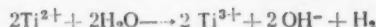
The yield of gaseous products increases with rise in reaction temperature and approximates to quantitative at 100° (on the basis of the weight of ethyllithium taken for reaction). It should be noted that even at low temperature the liberation of gas proceeded for several minutes. However, the mixture was always kept for a long time (several hours) to ensure completion of the reaction. Table 1 shows that the yields of gases at low temperatures are 10-20% and ethane predominates in their composition. From this it might be concluded that in these experiments ethylene liberated simultaneously with ethane is partially polymerized. However, in those experiments in which, after the separation of the gaseous products, the reaction mixture was decomposed with water, it was shown that the whole of the hydrocarbon part then separated as ethane and that the over-all yield of hydrocarbons was close to or equal to the theoretical value. Thus, in Expt. 1, which was carried out at 0°, 22% of the hydrocarbon part was liberated as reaction gas, and on decomposition of the precipitate a further 78% was obtained as ethane. In another experiment the reaction gas and the gas from the decomposition of the remaining reaction mixture were collected together. In this case the over-all yield of the hydrocarbon part was again almost 100% on the amount of ethyllithium taken for reaction. Here the gas contained 83% of ethane, 12% of ethylene, and 4% of butane.

It follows from the above that under these conditions there is no polymerization of the ethylene formed as a result of the reaction. At 100° and above it is necessary to take account of the possibility of the thermal decomposition of ethyllithium [9]. However, this process occurs incomparably more slowly than the decomposition of ethyllithium in its complex with titanium trichloride. The reaction of titanium trichloride with ethyllithium occurs almost instantly at 100°, whereas under these conditions the thermal decomposition of ethyllithium proceeds only to the extent of 25% in 14 hr. The composition of the gases formed in each of these cases is given in Table 2 for two characteristic experiments. The amount of titanium dichloride formed in various reactions is usually determined

TABLE 3. Amount of Hydrogen Liberated in the Hydrolysis of the Products of the Reaction of LiC_2H_5 with TiCl_3

No.	Molar ratio LiC_2H_5 per TiCl_3	Reaction time (hr)	Reaction temp. (°C)	Amt. of hydrogen(%)	
				LiC_2H_5	TiCl_3
1	1,0	3	0	41	93
2	2,3	72	20	28	130
3	1,5	6	55	59	180
4	3,5	6	55	73	500
5	1,8	4	100	70	256
6	6,0	12	100	78	960

[10, 11] from the amount of hydrogen liberated on hydrolysis of the precipitate. It was found that the reaction proceeds according to the scheme



We found that in the hydrolysis of the products formed as a result of the reaction of ethyllithium with titanium trichloride the amount of hydrogen liberated was sometimes several times as great as that to be expected from the stoichiometric equation (assuming that hydrogen is formed only on account of titanium dichloride). On hydrolysis of the precipitate (with water or weak hydrochloric acid) it passed into solution, which was a direct indication of the absence of metallic titanium in the reaction products.

Another source of hydrogen in the hydrolysis of the precipitate could be lithium hydride, which could be formed in the decomposition of ethyllithium in accordance with the scheme



Such decomposition does occur, but at temperatures of above 100°. As already stated above, in presence of titanium trichloride the decomposition of ethyllithium goes much more vigorously and at lower temperatures. At 55° and 100° this process goes rapidly, and in our experiments up to 7 moles of ethyllithium were decomposed per mole of titanium trichloride (Table 3).

From the data given it must be concluded that titanium halides catalyze the decomposition of ethyllithium to form lithium hydride and ethylene.

EXPERIMENTAL

Ethyllithium was prepared by the usual method in benzene solution in an argon or nitrogen atmosphere from lithium and ethyl chloride at 40°. Titanium trichloride was prepared from TiCl_4 by reduction in a stream of hydrogen at 800-900° in a tube fitted with a silit resistor. Excess of titanium tetrachloride was vacuum-distilled or washed with hexane from the crystalline violet α -modification of titanium trichloride formed. The solvents, i.e., nonane, benzene, and hexane, were purified with concentrated sulfuric acid and boiled and distilled over sodium in an atmosphere of inert gas.

Reaction of ethyllithium with titanium trichloride. The reaction was carried out in an apparatus assembled in accordance with the scheme represented in the figure. The ampoule (3) was first degassed; it was heated to 250-300° while under evacuation to 1-1.5 mm and then filled with inert gas; this operation was repeated 2-3 times. A benzene solution of ethyllithium (e.g., 20 ml containing 0.52 mole/liter) was transferred from the vessel (1) to the ampoule (3), benzene was vacuum-distilled off through the side tube (7), and a measured amount of nonane or hexane was transferred from the vessel (2) into the residue of crystalline ethyllithium. In a stream of argon a small ampoule containing titanium trichloride was attached to the side tube (7), and this was closed with the clip (5). With the tap (8) closed, the upper parts of the apparatus were connected, and in a stream of argon we connected these with the small spiral condenser (6), which was attached to a gas buret. The ampoule (3) containing the solution of ethyllithium in the necessary solvent was placed in a thermostat, the tap (8) and the clip (5) were opened, and ground titanium trichloride was passed in. Gas soon started to be evolved, and the solution and precipitate acquired a dark-green color. The introduction of the titanium trichloride took about five minutes. The mixture was kept at the required temperature until gas ceased to be evolved. The apparatus was then purged with argon with collection of the gas in the same buret.

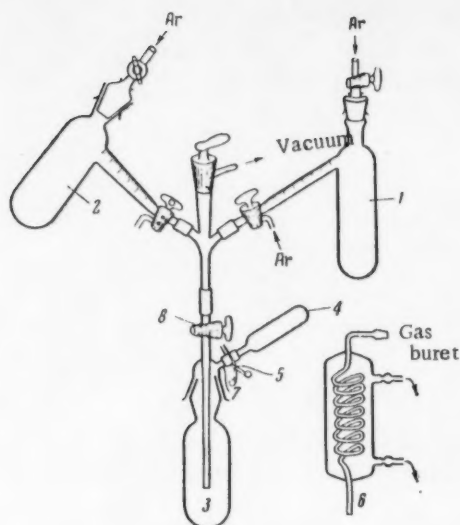


Diagram of apparatus: 1) Schlenk vessel containing ethyllithium; 2) Schlenk vessel containing nonane over sodium; 3) ampoule apparatus; 4) ampoule for TiCl_3 ; 5) clip; 6) spiral condenser; 7) side tube; 8) tap.

of C_4H_{10} . The remaining mixture was decomposed with weak hydrochloric acid, and in the gas liberated we found 32.5 ml of H_2 and 156 ml of C_2H_6 . Calculation showed that in this way 93% of all the hydrocarbon part of the ethyllithium taken for reaction had been accounted for.

The gas analysis was carried out as follows: 1) by the methods of gas-liquid chromatography; 2) by absorption of ethylene with a solution of mercury sulfate or bromine water, and combustion of hydrogen over palladized asbestos and of hydrocarbons over copper oxide.

SUMMARY

1. Ethyllithium reacts with titanium trichloride at low temperatures with formation of ethane, ethylene, and butane; the composition of the gas is determined by the relative amounts of the reactants.
2. Titanium halides catalyze the decomposition of ethyllithium into ethylene and lithium hydride.

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Decomposition of reaction products. After the separation of the gaseous reaction products, the tap (8) was closed, the condenser (6) and the gas buret were disconnected, and a T-piece similar to that used previously was connected. In a stream of argon the ampoule (4) was removed and the condenser (6) was attached to the side tube (7). Through the T-piece and the tap (8), water or weak hydrochloric acid was introduced. The gases liberated were collected and analyzed. In some experiments the precipitate was first washed as follows. With passage of argon through the tap (8) the upper part was removed at the ground joint from the ampoule (3), which was closed and centrifuged (4000 r.p.m., 30-40 min); the solution was decanted into a specially prepared ampoule, a fresh portion of solvent was added, the whole was shaken, and centrifugation was repeated. The precipitate, washed in this way, was treated with water as described above. In attempts to separate the precipitate by filtration it was shown that it was so finely dispersed that it was not retained by a porous glass filter.

Thermal decomposition of ethyllithium. For the decomposition we took 19.7 ml of ethyllithium (0.52 mole/liter) in benzene; the benzene was vacuum-distilled off and replaced by nonane. The ampoule was placed in a thermostat at 98°. In the course of 19 hr 49.6 ml of gas (STP) was liberated. The apparatus was purged with argon, and the gas was collected and analyzed. We found 34.8 ml of C_2H_4 , 7.3 ml of C_2H_6 , and 7.5 ml

UNSATURATED ACIDS CONTAINING TRIFLUOROMETHYL GROUPS

COMMUNICATION 1. POLARIZATION OF THE DOUBLE BOND

IN 3,3-BISTRIFLUOROMETHYLACRYLIC ACID

I. L. Knunyants and Yu. A. Cheburkov

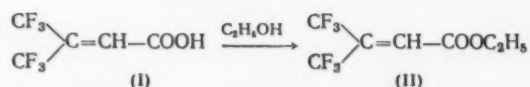
Institute of Heteroorganic Compounds, Academy of Sciences, USSR

Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

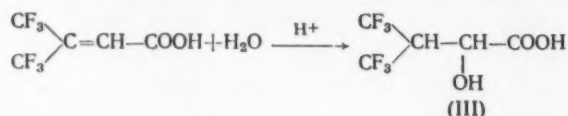
No. 12, pp. 2162-2167, December, 1960

Original article submitted July 2, 1959

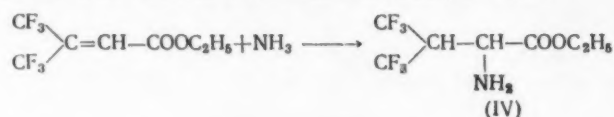
3,3-Bistrifluoromethylacrylic [4,4,4-trifluoro-3-(trifluoromethyl)crotonic] acid (I), which is prepared by the isomerization of β , β -bistrifluoromethyl- β -propiolactone [1], is readily esterified with ethanol with formation of the corresponding ester (II):



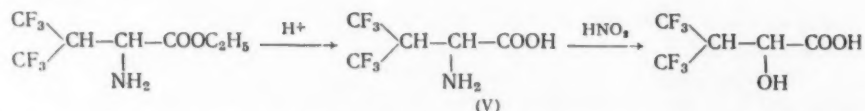
When heated with caustic alkali solution both the acid and its ester react with loss of fluorine atoms, but in an acid medium under severe conditions (200° under pressure) we succeeded in bringing about the addition of water to the acid (I). We then obtained 3,3-bistrifluoromethylactic [4,4,4-trifluoro-2-hydroxy-3-(trifluoromethyl)butyric] acid (III), which differed in its properties from the β -hydroxy acid described previously [1]:



Unlike water, ammonia added to the ester (II) under mild conditions (-80°) with formation of the ethyl ester of hexafluorovaline [ethyl 2-amino-4,4,4-trifluoro-3-(trifluoromethyl)butyrate] (IV):

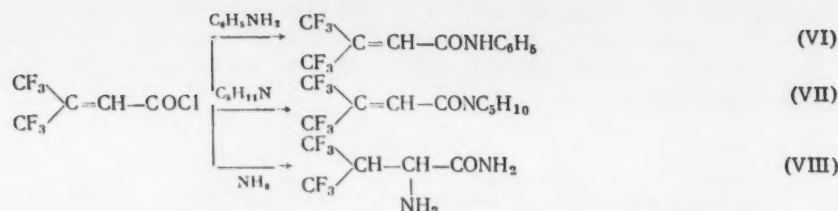


Its structure was proved by hydrolysis in an acid medium and conversion of the resulting hexafluorovaline (V) into the α -hydroxy acid (III):

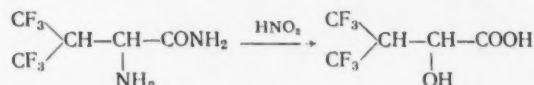


From the hexafluorovaline ester (IV) we were unable to obtain the amide of hexafluorovaline by the action of ammonia. In all cases (ammonia in ether, alcohol, or water; liquid ammonia) reaction occurred with removal of fluorine atoms from the molecule.

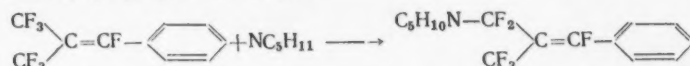
The amide of hexafluorovaline (VIII) was prepared from 3,3-bistrifluoromethylacryloyl chloride, and whereas aniline and piperidine react with the acid chloride with formation of the corresponding amides of 3,3-bistrifluoromethylacrylic acid (VI) and (VII), in addition ammonia also adds at the double bond:



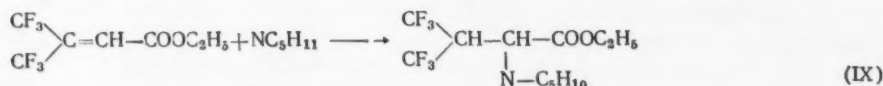
The structure of the amide (VIII) was proved by its conversion into the α -hydroxy acid (III) by the action of nitrous acid:



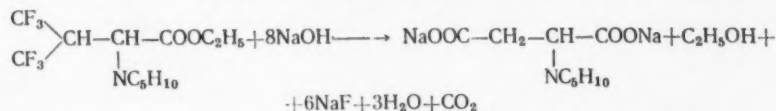
As shown previously, unlike ammonia, piperidine replaces a fluorine atom in the trifluoromethyl group of [tetrafluoro-2-(trifluoromethyl)propenyl]benzene [2]:



In the case of 3,3-bistrifluoromethylacrylic ester replacement in the trifluoromethyl group does not occur and, like ammonia, piperidine adds at the double bond with formation of 2-piperidino-3,3-bistrifluoromethylpropionic ester (IX):



The structure of the ester (IX) is confirmed not only by its analogy with the structure of the products of the addition of ammonia and water, but also by the ready removal of all fluorine atoms on alkaline hydrolysis:

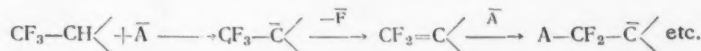


The ready hydrolysis in presence of bases of a trifluoromethyl group attached to a saturated carbon atom carrying at least one fairly mobile hydrogen atom is widely known in the literature. Thus, fluorine is readily hydrolyzed in diaryltrifluoroethane $\begin{array}{c} \text{Ar} \\ \diagup \\ \text{CH}-\text{CF}_3 \\ \diagdown \\ \text{Ar} \end{array}$ [3] and in ethyl 2-(trifluoromethyl)propionate $\begin{array}{c} \text{CF}_3 \\ \diagup \\ \text{CH}-\text{COOC}_2\text{H}_5 \\ \diagdown \\ \text{CH}_3 \end{array}$ [4]. On

the other hand, the trifluoromethyl group is stable and is not hydrolyzed in compounds in which an α -hydrogen atom is either absent, as in 1,1-diaryl-2,2,2-trifluoroethanols $\begin{array}{c} \text{Ar} \\ \diagup \\ \text{C}-\text{CF}_3 \\ \diagdown \quad | \\ \text{Ar} \quad \text{OH} \end{array}$ [5] and in ethyl 2-(trifluoromethyl)lactate

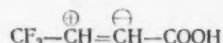
$\begin{array}{c} \text{CF}_3 \\ \diagup \\ \text{C}-\text{COOC}_2\text{H}_5 \\ \diagdown \quad | \\ \text{CH}_3 \quad \text{OH} \end{array}$, or of reduced mobility on account of the donation of electrons by a neighboring group, as in 2-(trifluoromethyl)-1-propanol or 2-(trifluoromethyl)propylamine $\begin{array}{c} \text{CF}_3 \\ \diagup \\ \text{CH}-\text{CH}_2\text{OH} \\ \diagdown \\ \text{CH}_3 \end{array}$, $\begin{array}{c} \text{CF}_3 \\ \diagup \\ \text{CH}-\text{CH}_2\text{NH}_2 \\ \diagdown \\ \text{CH}_3 \end{array}$ [4].

Hence, the mechanism proposed by McBee for the hydrolysis of the trifluoromethyl group in such compounds includes primary attack by the anion with elimination of a proton in the α -position [4]:

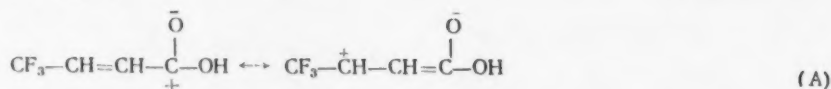


The hydrolysis of fluorine in the action of ammonia or caustic alkali on 3,3-bistrifluoromethylacrylic ester and acid, on hexafluorovaline ester, and on 3,3-bistrifluoromethylactic acid—all this forms an indirect confirmation of such a direction of addition of water, ammonia and piperidine to 3,3-bistrifluoromethylacrylic acid and its ester, in which there is hydrogen in the α -position to the trifluoromethyl groups.

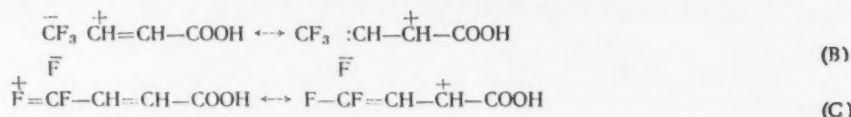
In 1953-56 there were studies of the addition of water, ammonia, and hydrogen bromide to 4,4,4-trifluorocrotonic acid and its ester [6, 7, 8]. It was found that in the competing effects on the double bond of two electron-accepting groups (trifluoromethyl and carboxyl) the latter was the stronger and this determined the direction of addition to trifluorocrotonic acid:



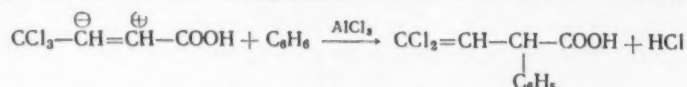
The electron displacement in trifluorocrotonic acid can be represented by the valence structures (A), which express the electromeric effect of the carboxy group:



In the appraisal of the effect of the trifluoromethyl group it is necessary to take account both of the powerful induction effect (B), and also of hyperconjugation with participation of fluorine (C) [9, 10]:



In the case of fluorine hyperconjugation must greater significance than in the case of hydrogen on account of the high electronegativity of fluorine, but less significance than in the case of chlorine because of the high stability and low polarizability of the C-F bond. It is here that we find the explanation of the apparent contradictions in the behavior of the trichloromethyl group. It is known that the induction effect of the trichloromethyl group is less than that of the trifluoromethyl group (trichloroacetic acid is weaker than trifluoroacetic acid), but the direction of the addition of benzene to trichlorocrotonic acid, which was studied by Nesmeyanov, Freidlina, and Zakharkin [11], was found to be opposite to that of the addition of ammonia and hydrogen bromide to trifluorocrotonic acid, which would appear to point to the opposite direction of the polarization of the double bond in this compound:

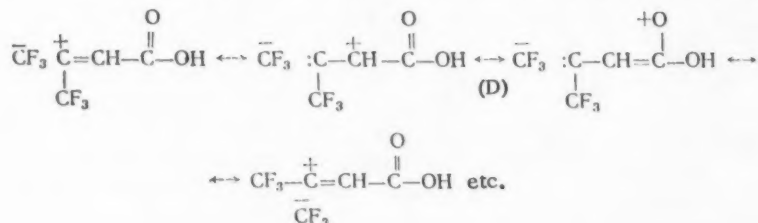


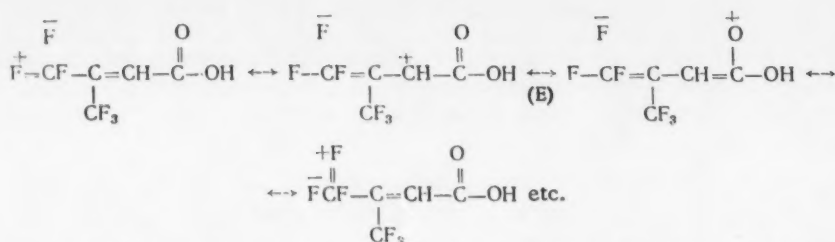
However, this fact is possibly to be explained on the view that the electromeric effect of the carboxyl is opposed also by the dynamic inductomeric ($-I_d$) effect of the trichloromethyl group, which is manifested in the allyl rearrangement; in trichlorocrotonic acid valence structures of type (C) are more important than those of the type (B):



On the other hand, the absence of products of the allyl rearrangement in addition reactions with trifluorocrotonic acid indicates that in this case valence structures of type (B) may be of greater importance.

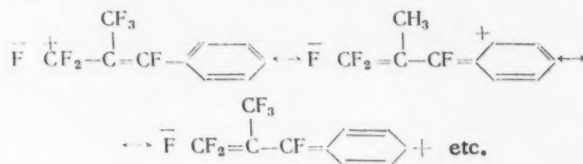
In the case of 3,3-bistrifluoromethylacrylic acid, the effect of the carboxyl is opposed by not one, but two trifluoromethyl groups. It is found that the direction of the polarization of the double bond becomes the reverse to that in trifluorocrotonic acid, and the displacement of electrons in 3,3-bistrifluoromethylacrylic acid may be represented by the structures (D) and (E) in accordance with the two mechanisms of the effect of the trifluoromethyl group:





The exhaustion of the double bond by the trifluoromethyl groups hinders the donation of electrons in the direction of carboxyl; consequently, the reaction of electrophilic addition starting with an attack of the oxygen of the carbonyl group with a proton must be made very difficult, which is in fact observed in the addition of water in an acid medium.

On the other hand, the lowering of the electron density of the double bond due to the effect of the carboxyl makes the fluorine atoms in the trifluoromethyl group considerably less mobile than in the case of [tetrafluoro-2-(trifluoromethyl) propenyl]-arenes and -alkanes, in which the increase in the electron density of the double bond by the electron-donating substituent facilitates the departure of the fluorine as an anion:



The absence of products of allyl rearrangement in nucleophilic additions to 3,3-bistrifluoromethylacrylic acid and its ester indicates that in this case, as in the case of trifluorocrotonic acid, a considerable contribution is made by the structure (D), which takes account of the induction ($-I_s$) effect of the trifluoromethyl group.

The explanation that we have given is not the only one possible as we have taken no account at all of steric factors, which may be of great importance.

EXPERIMENTAL

Ethyl 3,3-bistrifluoromethylacrylate (II). This was prepared in the usual way in 81% yield from the acid (I) and absolute alcohol in presence of concentrated H_2SO_4 ; b.p. 128° (747 mm); n_D^{20} 1.3414; d_4^{20} 1.3525; found MR 36.72. $\text{C}_7\text{F}_6\text{H}_6\text{O}_2$. Calculated MR 36.55 at Ar_F 1.24. Found: C 36.03; H 2.67; F 47.77%. Calculated: C 35.60; H 2.54; F 48.20%.

3,3-Bistrifluoromethylactic acid (III). A glass ampoule was charged with 1 g of the acid (I) and 2 ml of 0.15% sulfuric acid, and the mixture was heated for ten hours at $190-200^\circ$; the solution was filtered and extracted with ether. After evaporation of ether we obtained 0.6 g (55%) of crystals. Recrystallization from CCl_4 gave an acid of m.p. $99.5-99.8^\circ$. Found: C 27.02; H 1.74; F 50.51%. $\text{C}_6\text{F}_6\text{H}_4\text{O}_3$. Calculated: C 26.50; H 1.77; F 50.40%.

The amino ester (IV) (0.42 g) was boiled with 2 ml of 30% sulfuric acid until, on cooling, there was no precipitate of the amino ester sulfate, which is insoluble in water. The solution was then diazotized, and the liquid layer (0.17 g) which then formed was separated. After extraction and evaporation of the ether we obtained 0.17 g (47%) of an acid, which was identical with that obtained in the preceding experiment; m.p. $100.5-101^\circ$.

Hexafluorovaline ethyl ester (IV). Ammonia was passed into a flask containing 4.94 g (0.02 mole) of the ester (II) in 10 ml of dry ether at -80° . The solution was filtered, ether was distilled off, and the residue was twice vacuum-distilled. We obtained 4.26 g (80%) of (IV); b.p. $77.0-77.2^\circ$ (20 mm); n_D^{20} 1.3592; d_4^{20} 1.410; found MR 39.52 $\text{C}_7\text{F}_6\text{H}_9\text{O}_2\text{N}$. Calculated MR 39.72 at Ar_F 1.12. Found: C 33.05; H 3.58; F 45.14%. Calculated: C 33.20; H 3.56; F 45.01%.

The hydrochloride is insoluble in water; m.p. 184° (decomp.); it was purified by sublimation. Found: Cl 12.20; N 4.86%. $\text{C}_7\text{F}_6\text{H}_{10}\text{O}_2\text{NCl}$. Calculated: Cl 12.26; N 4.84%. After hydrolysis of a small test sample of the ester with 0.1 N KOH and neutralization to litmus, the solution gave a color with ninhydrin.

The ester (II) (1.46 g), when shaken with concentrated ammonia solution at 0° for eight hours with subsequent extraction, drying, and distillation, gave 1 g (64%) of the ester (IV), b.p. 77-79° (20 mm).

Hexafluorovaline (V). This was prepared in 91% yield by boiling the ester (IV) with 20% hydrochloric acid for ten hours with subsequent evaporation of the solution to dryness and crystallization of the residue from alcohol; m.p. 204° (decomp.); neutralization equivalent: found 219, calculated 211. Found: C 26.71; H 2.35; F 49.93; N 6.15%. $C_5F_6H_5O_2N$. Calculated: C 26, 70; H 2.21; F 50.63; N 6.22%.

3,3-Bistrifluoromethylacrylanilide (IV). This was prepared in 95% yield from the acid chloride* and aniline at -80°; m.p. 114-114.5° (from CCl_4). Found: C 46.74; H 2.67; F 39.93; N 5.03%. $C_{11}F_6H_7ON$. Calculated: C 46.64; H 2.47; F 40.28; N 4.96%.

Piperidide of 3,3-bistrifluoromethylacrylic acid (VII). This was prepared in 56% yield from the acid chloride and piperidine; m.p. 44.5-45° (from hexane). Found: C 43.64; H 3.99; F 41.84; N 5.28%. $C_{10}F_6H_{11}ON$. Calculated: C 43.63; H 4.00; F 41.4; N 5.09%.

Amide of hexafluorovaline (VIII). This was prepared in 66% yield from the acid chloride and ammonia in ether at 0°; m.p. 61.5-63° (from CCl_4). Found: C 26.72; H 2.67; F 50.97; N 12.36%. $C_5F_6H_5ON_2$. Calculated: C 26.78; H 2.67; F 50.89; N 12.54%. The amide (VIII) (0.28 g) was diazotized at 0° in 40% sulfuric acid. The solution was separated from oil and extracted with ether. After evaporation of the ether we obtained 90 mg (30%) of the acid (III), m.p. 97.5-100°.

Ethyl 2-piperidino-3,3-bistrifluoromethylpropionate (IX). Dropwise addition was made of 7.6 g (0.089 mole) of piperidine to a solution of 10.1 g (0.043 mole) of the ester (II) in 80 ml of dry ether at 0°. On the next day the solution was poured from the precipitate and ether and excess of piperidine were removed in a vacuum. Distillation of the residue gave 9.9 g (72%) of crystals, m.p. 26.5-27.5° (from alcohol). Found: C 45.33; H 5.44; F 35.36; N 4.38%. $C_{12}F_6H_{17}O_2N$. Calculated: C 44.86; H 5.29; F 35.51; N 4.35%.

Hydrolysis of the ester (IX). The ester (IX) (0.5618 g) was refluxed for five hours with 20 ml of alcoholic NaOH containing 0.07314 g of NaOH in 1 ml. The solution was transferred to a 100-ml flask and made up to the mark with water. In the titration of 5 ml of the solution obtained 6.2 ml of 0.1 N H_2SO_4 was required, and in the titration of 1 ml of the solution 4.50 ml of 0.025 N $Th(NO_3)_2$ was required; $K = 0.9878$. From these data it was calculated that 7.849 moles of NaOH was consumed per mole of the ester, and 6.300 g-ions of fluorine was liberated.

SUMMARY

The addition of water, ammonia, and piperidine to 3,3-bistrifluoromethylacrylic acid and its ester was carried out and led to the formation of 2-substituted 3,3-bistrifluoromethylpropionic acids. This indicates that the polarization of the double bond in 3,3-bistrifluoromethylacrylic acid is in the reverse direction to that in trifluorocrotonic acid.

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*For the preparation of 3,3-bistrifluoromethylacryloyl chloride see the following communication.

UNSATURATED ACIDS CONTAINING TRIFLUOROMETHYL GROUPS
COMMUNICATION 2. FREE-RADICAL ADDITION OF HYDROGEN BROMIDE
TO 3,3-BISTRIFLUOROMETHYLACRYLIC ACID

I. L. Knunyants and Yu. A. Cheburkov

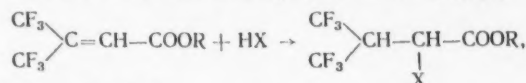
Institute of Heteroorganic Compounds, Academy of Sciences, USSR

Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 12, pp. 2168-2172, December, 1960

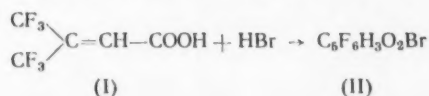
Original article submitted July 2, 1959

The preceding paper was concerned with the ionic addition of ammonia, water, and piperidine to 3,3-bistrifluoromethylacrylic acid [4, 4,4-trifluoro-3-(trifluoromethyl)crotonic acid] (I) [1]:



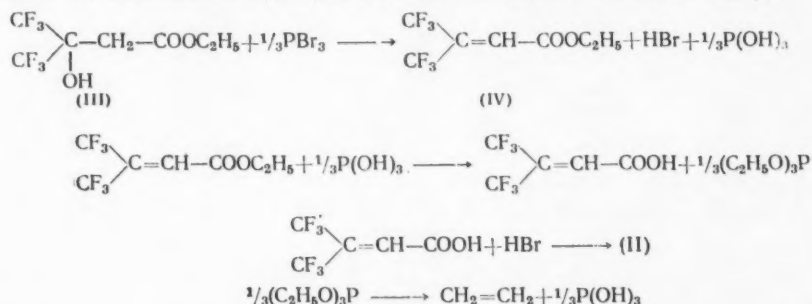
in which R = H or C₂H₅; X = OH, NH₂, or NC₅H₁₀.

Dry hydrogen bromide, both under conditions favoring free-radical reaction and in absence of initiator (in presence of inhibitor), adds to the acid (I) giving a high yield of only one product, bromo-3,3-bistrifluoromethylpropionic acid (II):

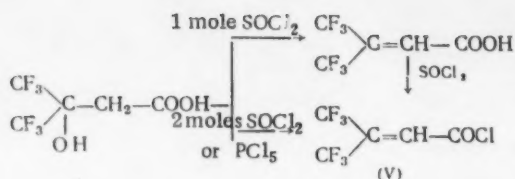


It is evident that, even in presence of an inhibitor, the reaction has a free-radical mechanism for in this case it necessary to work at a high temperature, at which the thermal decomposition of hydrogen bromide into free radicals is possible [2].

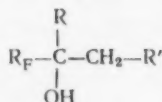
In order to prove the structure of the bromo acid (II) an attempt was made to replace hydroxyl by bromine in ethyl 3-hydroxy-3,3-bistrifluoromethylpropionate (III), which we prepared earlier [3]. It was found that this ester reacts with phosphorus tribromide only under such severe conditions (in a sealed tube at 190°) that as a result of dehydration we obtained 3,3-bistrifluoromethylacrylic acid, its ester (IV), and the bromo acid (II):



In presence of pyridine thionyl chloride reacted similarly to phosphorus tribromide with the hydroxy ester (III). On reaction with one molecular proportion of thionyl chloride, 3-hydroxy-3,3-bistrifluoromethylpropionic acid is dehydrated with formation of 3,3-bistrifluoromethylacrylic acid, and with two molecular proportions of thionyl chloride or phosphorus pentachloride the product is 3,3-bistrifluoromethylacryloyl chloride (V), identical to the acid chloride prepared from the acid (I) and thionyl chloride:

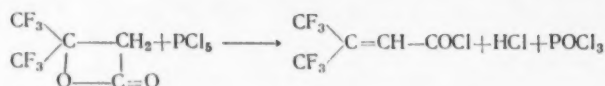


The elimination of water from the hydroxy ester (III) by means of thionyl chloride under relatively mild conditions is not altogether a usual reaction, for it is well known that compounds of the following general formula are difficult to dehydrate:

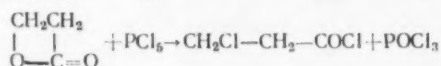


For example, 3,3,4,4,4-pentafluoro-2-methyl-2-butanol is dehydrated over phosphorus pentoxide only at 275° [4], ethyl 3-hydroxy-3,3-bistrifluoromethylpropionate does not lose water when heated with phosphorus pentoxide at 280° [5], and 1,1,1-trifluoro-2-octanol could not be dehydrated over alumina at 350° and over phosphorus pentoxide at 253° [6]. Thus, attempts to replace hydroxyl by halogen in 3-hydroxy-3,3-bistrifluoromethylpropionic acid and its ester were not successful.

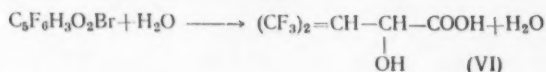
Another method of introducing halogen into the β -position to carboxyl, namely the action of phosphorus pentachloride on β , β -bistrifluoromethyl- β -propiolactone, also led to the formation of 3,3-bistrifluoromethylacryloyl chloride.



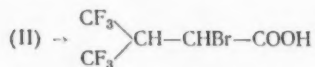
whereas in this reaction fluorine-free β -lactones give the substituted 3-chloropropionic acid [7].



The structure of the bromo acid (II) was proved by hydrolysis of the halogen at 135° with water in a sealed tube. We then obtained 3,3-bistrifluoromethylactic acid (VI), identical to the product described in the preceding communication [1]:



Hence, the product of the addition of hydrogen bromide to 3,3-bistrifluoromethylacrylic acid is 2-bromo-3,3-bistrifluoromethylpropionic acid:

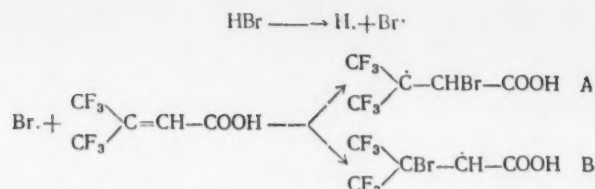


Under these conditions 3,3-bistrifluoromethylacrylic acid does not react with aqueous hydrogen bromide, which proves that hydrolysis does not proceed by preliminary elimination of hydrogen bromide and subsequent addition of water.



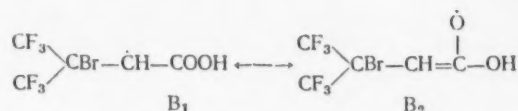
When hydrolysis is carried out in an alkaline medium replacement of the fluorine occurs, which is an indirect confirmation of the indicated direction of the addition of hydrogen bromide.

The addition of hydrogen bromide to 3,3-bistrifluoromethylacrylic acid is a free-radical process; the reaction is catalyzed by peroxide and ultraviolet radiation and is inhibited by hydroquinone. Of the two possible intermediate radicals A and B obtained in the attack of the double bond of the acid by the bromine radical, the free radical A is the more stable:



This is in accord with data on the high stability of fluorine-containing tertiary radicals, as compared with secondary and primary radicals [8, 9].

Hence, the branching of the carbon chain stabilizes the radical A to a greater extent than resonance between the two structures B₁ and B₂



stabilizes the radical B.

EXPERIMENTAL

2-Bromo-3,3-bistrifluoromethylpropionic acid (II). A mixture of 3.87 g (0.0185 mole) of the acid (I), 2.5 g (0.031 mole) of hydrogen bromide, and 0.02 g of benzoyl peroxide was sealed in a quartz ampoule, and the mixture was subjected to ultraviolet radiation at 40° for 12 hr. We obtained 5.21 g (97%) of an acid, m.p. 67-68° (from hexane). Found: C 21.16; H 1.01; F 38.76%. C₅F₆H₃O₂Br. Calculated: C 20.8; H 1.04; F 39.40%. Neutralization equivalent: found 282; calculated 289.

In a control experiment in which the peroxide was absent and the mixture was left in the dark at 40°, unchanged acid (I) was isolated.

A mixture of 3.92 g (0.0188 mole) of the acid (I) which had been freshly distilled in a stream of nitrogen over hydroquinone, 1.92 g (0.0237 mole) of hydrogen bromide, and 0.03 g of hydroquinone was introduced in an atmosphere of nitrogen into a glass ampoule. The ampoule was cooled with liquid nitrogen and evacuated to a residual pressure of 0.1 mm, sealed, and heated at 100° for ten hours (at 50° reaction did not go). We isolated 5.44 g (quantitative yield) of the acid (II), identical with the sample obtained in the first experiment.

Reaction of ethyl 3-hydroxy-3,3-bistrifluoromethylpropionate with phosphorus tribromide. A mixture of 8.4 g (0.033 mole) of the ester (III) and 5.14 g (0.019 mole) of PBr₃ was heated in a sealed ampoule at 180-190° until the layer of phosphorus tribromide disappeared completely (16 hr). When the ampoule was opened a gas was liberated which decolorized bromine water and permanganate solution. The liquid was poured from the solid precipitate and treated with bicarbonate. The residual oil was taken up in ether, dried, and fractionated through a column. We obtained 2.03 g (26%) of the ester (IV), b.p. 127-128° (746 mm) and n_D²⁰ 1.3400, identical with the product described previously [1]. The acid precipitated on acidification of the bicarbonate solution was crystallized from hexane, and we obtained 2 g (21%) of the acid (II), m.p. 66-67°. Distillation of the mother liquor gave 1.9 g (27%) of the acid (I), b.p. 159-163° (751 mm), identical with the product described previously [3].

Ethyl 3,3-bistrifluoromethylacrylate (IV). A mixture of 20.83 g (0.082 mole) of the ester (III) and 13.3 g (0.110 mole) of thionyl chloride in 30 ml of dry pyridine was heated at 100° for seven hours in a flask fitted with reflux condenser. The liquid was then diluted with ether, and was washed, dried, and distilled; we obtained 7.85 g (40%) of the ester (IV), b.p. 127-129° and n_D²⁰ 1.3405.

3,3-Bistrifluoromethylacryloyl chloride (V). This was prepared in 86% yield from the acid (I) and thionyl chloride in presence of a catalytic amount of pyridine. It does not react with water, and is slowly hydrolyzed by sodium carbonate solution (10 g dissolved in 20% sodium carbonate solution in the course of one month). B.p. 85.3°-85.5° (741 mm); n_D²⁰ 1.3421; d₄²⁰ 1.536; found MR 31.09. C₅F₆HOC₂Cl. Calculated MR 30.81 (AR_F taken as 1.24). Found: C 26.96; H 0.50; F 49.93%. Calculated: C 26.4; H 0.44; F 50.3%.

When phosphorus trichloride is used, heating must be at 140° for eight hours; the yield then falls to 60%.

In order to prepare the acid chloride from 3-hydroxy-3,3-bistrifluoromethylpropionic acid, a mixture of 11.11 g (0.049 mole) of the hydroxy acid, 11.5 g (0.097 mole) of thionyl chloride, and 0.5 ml of pyridine was heated at 80° for six hours in a flask fitted with reflux condenser. Distillation of the mixture gave 7.3 g (65%) of the acid chloride (V), b.p. 80-86°. The anilide had m.p. 111-113° and was identical with the sample described in the preceding communication [1].

With equimolecular proportions of the hydroxy acid and thionyl chloride we obtained the acid (I), b.p. 155-157°, in 60% yield.

When 2 moles of PCl_5 was used per mole of the hydroxy acid, the yield of (V) was 44%.

For the preparation of the acid chloride from β,β -bistrifluoromethyl- β -propiolactone, a mixture of 21 g (0.1 mole) of the lactone and 23 g (0.11 mole) of PCl_5 was heated in a sealed tube at 160-180° until the whole of the PCl_5 had dissolved (about 30 hr). The mixture was then fractionated through a column. We obtained: Fraction 1, b.p. 69-70°; 3.8 g of an azeotropic mixture consisting of 50% of the acid chloride (V) and 50% of PCl_3 ; when cooled to -80° it separated into layers, and on hydrolysis it gave phosphorous acid, detected by the reduction of mercuric chloride to calomel in the cold and to metallic mercury on heating. Fraction 2, b.p. 86-87.5° and n_D^{20} 1.3405; 12.7 g (56%) of the acid chloride (V). Fraction 3, b.p. 103-106°; 9 g of phosphoryl chloride. Fraction 4, b.p. 113-120°; 4 g of residue, which was not investigated further.

3,3-Bistrifluoromethylactic acid (VI). A mixture of 0.49 g (0.0017 mole) of the acid (II) and 4 ml of water was heated at 135° in a sealed tube until the acid dissolved (20 hr). After extraction and evaporation of ether we obtained 0.2 g (52%) of the acid (VI), m.p. 99-101.5° (from CCl_4), identical with the sample described in the preceding communication [1].

In a control experiment we took 0.46 g (0.0022 mole) of the acid (I) and 4 ml of water containing 0.17 g (0.0021 mole) of hydrogen bromide. After 24 hr at 135° the acid had not dissolved.

SUMMARY

1. The free-radical addition of hydrogen bromide to 3,3-bistrifluoromethylacrylic acid was carried out. Like the ionic addition of water and amines, this leads to the formation of an α -substituted 3,3-bistrifluoromethylpropionic acid.
2. It was shown that 3-hydroxy-3,3-bistrifluoromethylpropionic acid and its ester are readily dehydrated under the action of thionyl chloride and phosphorus halides.

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COMPOSITIONS OF THE PRODUCTS OF THE DEHYDROGENATION OF C₆-C₉ n-ALKANES OVER AN ALUMINA-CHROMIA-POTASSIA CATALYST

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No. 12, pp. 2173-2177, December, 1960
Original article submitted July 10, 1959

In our previous investigation [1] on the transformations of the higher alkanes in presence of an alumina-chromia-potassia catalyst of composition Al₂O₃ 90.7 moles %, Cr₂O₃ 5.6 moles %, K₂O 3.7 moles %, we showed that at 500° with a space velocity of 0.5 hr⁻¹ from hexane, heptane, octane, and nonane, we obtained catalyzates containing 9-14% of unsaturated hydrocarbons and 39-50% of aromatics. The present investigation is devoted to a study of the structures of the unsaturated and aromatic hydrocarbons formed under these conditions with main emphasis on the investigation of the compositions of the olefins.

Data in the literature on this matter is incomplete. Only in the work of Hoog and co-workers [2] is it indicated that in the aromatization of hexane, heptane, and octane over chromic oxide at 475° alkenes are formed in which the double bond is toward the center of the molecule (3-hexene, 3-heptene, 3-octene). The compositions of the aromatic hydrocarbons formed in the dehydrocyclization of n-alkanes have been studied in greater detail. The most important investigations in this direction are those of Hoog [2] already mentioned and also the work of Herington and Rideal [3]. Hoog states that the only product of the aromatization of hexane is benzene, and of the aromatization of heptane is toluene. However, with increase in the molecular weight of the n-alkane the composition of the aromatic hydrocarbons formed becomes more complex. Thus, the octane catalyzate contains not only ethylbenzene, but also the isomeric xylenes. Moreover, small amounts of toluene are present. Herington and Rideal, who studied the composition of the aromatic hydrocarbons formed from nonane over an alumina-chromia catalyst at 475°, found that they consist of o-ethyltoluene (75%) and propylbenzene (25%).

In the transformations of C₆ n-alkanes and higher n-alkanes over oxide catalysts, dehydrocyclization has been the principal object of study. The alkenes obtained at the same time were regarded as undesirable products, and it was therefore natural that little attention was given to them. We, on the other hand, are concerned with the dehydrogenation of alkenes, and it was therefore of interest to us to investigate the structures of the alkenes formed from the higher n-alkanes in presence of a typical dehydrogenation catalyst that had previously been shown to have high activity in the dehydrogenation of C₅ paraffins [4]. It was important to determine whether the alkenes obtained corresponded in number of carbon atoms to the original n-alkanes and to determine the position of the double bond. At the same time we also investigated the structures of the aromatic hydrocarbons formed in the catalytic process.

TABLE 1. Properties of n-Alkane Catalyzates

Hydrocarbon	Yield of catalyzate (%)	n _D ²⁰	Iodine value	Content (%) in catalyzate of		Amt. of gas (liters at STP)	Composition of gas (% by vol.)		
				un-saturateds	aromatics		H ₂	C _n H _{2n}	C _n H _{2n+2}
Hexane	86,8	1,4220	41,5	13,7	42,6	34,400	95,0	0,6	4,4
Heptane	87,9	1,4370	23,6	9,1	47,0	33,120	92,5	0,5	7,0
Octane	85,2	1,4502	17,8	7,8	50,2	34,000	92,0	0,2	7,8
Nonane	83,3	1,4460	27,3	13,5	39,0	29,500	87,5	2,1	10,4

TABLE 2. Compositions and Properties of Fractions of Hexane Catalyzate

Fraction	Boiling range (°C)	Yield (% by vol.)	n_D^{20}	d_4^{20}	Iodine value	Alkene content (%)	Aromatic content (%) *	Results of analysis	
								with the aid of Raman spectra	by gas-liquid chromatography
I	42,5—67,7	46,0	1,3822	0,6705	82,9	27,4	Traces	Hexane, 3-hexene (trans), traces of 2-hexene (trans) and benzene	Hexane ~59%, pentane 1,5%, 2-Hexene } 20%, 2-pentene 0,5%, 3-Hexene } possibly 1-hexene ** (~7%) 3-Methylpentane 6% 2-Methylpentane 6%
II	67,7—68,6	45,8	1,3830	0,6732	43,7	14,4	2,5	Hexane, 2-hexene (trans) 8%, 3-hexene (trans) 7%, - benzene	Hexane 82,5%, 2-Hexene } 14,5%, 3-Hexene } Benzene 3%
III	68,6—84,5	37,3	1,4860	0,8556	24,8	8,2	87,5	Benzene, 2,4-hexadiene	2-Hexene } 5%, Hexane 3,5%, 3-Hexene } 2,4-Hexadiene 0,5% Benzene 90%
Residue		0,3	Not analyzed						

* Analysis by the relative-dispersion method.

** The presence of an olefin with a double bond at the end of the chain was confirmed also by infrared spectroscopy.

TABLE 3. Compositions and Properties of Fractions of Heptane Catalyzate

Fraction	Boiling range (°C)	Yield (%) by vol.)	n_D^{20}	d_4^{20}	Iodine value	Alkene content (%)	Aromatics content (%) *	Results of analysis with aid of Raman spectra
I	65.2-97.6	4.0	1.4100	0.6952	51.5	19.8	19.2	Heptane, 2-heptene (cis and trans), benzene
II	97.6-102.6	54.5	1.4010	0.7028	31.9	12.3	14.0	Heptane, 2-heptene (cis) 4%, 2-heptene (trans) 8%, toluene 12%, heptadiene
III	102.6-110.6	39.0	1.4900	0.8417	4.3	1.6	94.0	Toluene, heptadiene
Residue		1.5	Not analyzed					

TABLE 4. Compositions and Properties of Fractions of Octane Catalyzate

Fraction	Boiling range (°C)	Yield (%) by vol.)	n_D^{20}	d_4^{20}	Iodine value	Alkene content (%)	Aromatics content (%)	Results of analysis with aid of Raman spectra
I	35.1-108.3	3.5	1.4480	0.7831	66.3	29.2	52.8	Benzene, 4-octene (cis and trans)
II	108.3-121.3	5.1	1.4445	0.7829	30.8	13.6	46.4	Octane, toluene, 4-octene (trans)
III	121.3-126.2	35.0	1.4045	0.7147	23.7	10.5	1.0	Octane, 4-octene (cis and trans), toluene
IV	126.2-135.0	22.7	1.4495	0.7886	16.5	7.3	47.0	m-Xylene, possibly 2,4-octadiene, octane
V	135.0-142.5	23.0	1.5000	0.8718	5.0	2.2	87.5	o-Xylene 60%, ethylbenzene 22%, p-xylene 4%
VI	142.5	9.0	1.5050	0.8801	4.0	1.8	92.0	o-Xylene
Residue		0.4	Not analyzed					

EXPERIMENTAL

The n-alkane catalyzates were obtained in presence of the alumina-chromia-potassia catalyst at 500° with a space velocity of 0.5 hr⁻¹. In each experiment 100 ml of hydrocarbon was passed over a layer of 30 ml of catalyst. The properties of the catalysts are given in Table 1.

All the catalyzates were fractionated through a column of 40-plate efficiency. For the fractionation we took 400 ml of the hexane catalyzate and 100 ml each of the catalyzates of the other alkanes. The fractions were analyzed with the aid of Raman spectra. In addition, for the analysis of fractions of the hexane catalyzate we used gas-liquid chromatography in the apparatus described previously [5]. As filling we used kieselguhr impregnated with hexadecane or bis-2-ethylhexyl phthalate.

TABLE 5. Compositions and Properties of Fractions of Nonane Catalyzate

Fraction	Boiling range (°C)	Yield (% by vol.)	n_D^{20}	d_4^{20}	Iodine value	Alkene content (%)	Aromatics content (%)	Results of analysis with aid of Raman spectra
I	42.0-102.5	5.0	1.4250	0.7481	70.3	35.2	50.0	—
II	106.0-136.0	6.0	1.4788	0.8437	15.4	6.8	80.6	Toluene
III	136.0-147.5	15.0	1.4100	0.7468	36.2	18.0	18.0	Nonane, 4-nonene; ethylbenzene and o-xylene in ratio 4 : 1
IV	147.5-157.0	48.2	1.4125	0.7700	16.2	8.1	4.5	Nonane, propyl- benzene, cumene, 4-nonene, nona- diene
V	157.0-163.0	22.2	1.4967	0.8669	10.6	5.2	78.0	o- and m-methyl- toluenes in ratio 1 : 1
VI	163.0-167.0	5.8	1.5203	0.8952	33.6	16.2	84.0	o-ethyltoluene and 1,2,3-tri- methylbenzene in ratio 1 : 1
Residue		0.5	Not analyzed					

Hexane catalyzate. Table 2 gives the results of the analysis of fractions of the hexane catalyzate. It will be seen from this table that the alkenes formed in the catalytic process consisted mainly of hexenes, of which about 88% was 2-hexene and 3-hexene, 8% was 1-hexene, and 4% was 2,4-hexadiene. The only aromatic hydrocarbon detected was benzene. The catalyzate was found to contain also very small amounts (about 2% in all) of isomerization and cracking products of hexane, namely 2- and 3-methylpentanes, pentane, and 2-pentene.

Heptane catalyzate. As Table 3 shows, the alkenes formed from heptane consisted mainly of 2-heptene. Heptadiene, probably 2,5-heptadiene, was also present. The only aromatic hydrocarbon detected was toluene. Judging from the fractionation results there was only a small amount of cracking products; the first fraction amounted to only 4% of the whole catalyzate.

Octane catalyzate. As Table 4 shows, the only alkene found in the catalyzate was 4-octene. In addition we found a little more than 1% of octadiene, probably 2,4-octadiene. The aromatic hydrocarbons obtained consisted mainly of o- and m-xylenes and ethylbenzene. p-Xylene was also present in small amounts. Lower-boiling aromatic hydrocarbons were also detected, namely benzene and toluene in a total amount of about 5% on the catalyzate.

Nonane catalyzate. Table 5 shows that the only alkene in the catalyzate was 4-nonene. A nonadiene of unknown structure was also present. Of C_9 aromatic hydrocarbons we detected o- and m-ethyltoluenes, and 1,2,3-trimethyl-, propyl-, and isopropyl-benzenes were also present. The aromatic part of the catalyzate contained a fairly considerable amount (about 25% of all the aromatic hydrocarbons) of C_8 and lower hydrocarbons, including toluene, ethylbenzene, and possibly benzene.

Hence, as a result of this investigation it may be stated that the bulk of the unsaturated hydrocarbons formed from the n-alkanes consisted of alkenes corresponding in number of carbon atoms to the original alkanes and having the double bond in the 2-, 3-, or 4-position. In the hexane catalyzate we found also 1-hexene, though in much less amount than 2- and 3-hexenes. The possibility cannot be excluded that in the heptane, octane, and nonane catalyzates there were alkenes present other than the 2-heptene, 4-octene, and 4-nonene found, but they were so small in amount that they could not be detected with the aid of Raman spectra. In all the catalyzates we found dienes, the structures of which we did not succeed in establishing with certainty. The composition of the aromatic hydrocarbons formed from n-alkanes becomes more complex with increase in the molecular weight of the n-alkane;

hexane gives benzene, and heptane gives toluene, but octane gives mainly xylenes and ethylbenzene together with lower-boiling aromatic hydrocarbons, and nonane gives mainly ethyltoluenes, trimethylbenzene, propylbenzene, and cumene, but also lower-boiling hydrocarbons: benzene, toluene, and ethylbenzene.

SUMMARY

1. An investigation was made of the structures of the alkenes and aromatic hydrocarbons formed in the transformations of C_6 - C_9 n-alkanes in presence of an alumina-chromia-potassia catalyst at 500° at a space velocity of 0.5 hr^{-1} .
2. The bulk of the alkenes formed corresponded in number of carbon atoms to the original hydrocarbons. The double bond occurred mainly in the 2-, 3-, or 4-position.
3. In the catalyzates of all the n-alkanes small amounts of dienes were found.
4. The bulk of the aromatic hydrocarbons formed corresponded in number of carbon atoms to the original alkanes. In addition, the octane and nonane catalyzates contained some lower-boiling aromatic hydrocarbons.

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PREPARATION OF CYCLOHEPTATRIENE

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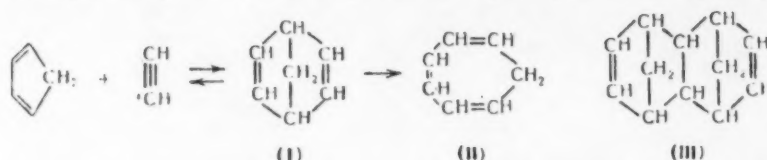
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In a study of the condensation of cyclopentadiene with acetylene [1, 2] with formation of 2,5-norbornadiene (I), the starting material for the manufacture of the insecticide aldrin, we noted that with rise in reaction temperature the yield of (I) rises at first and then, after passing through a maximum, begins to fall. As there is a simultaneous increase in the amount of products boiling higher than (I), it was natural to suppose that the reduction in the yield of norbornadiene might be explained by its isomerization at high temperature into cycloheptatriene (II) [2-6].



It was therefore of interest to investigate the possibility of preparing cycloheptatriene in one stage from cyclopentadiene and acetylene without isolation of the intermediately formed norbornadiene, and this formed the object of the present work. In fact, by rise in reaction temperature and increase in contact time, from cyclopentadiene and acetylene we obtained a mixture containing cycloheptatriene (yield about 20%) together with norbornadiene (yield 20-25%). We studied also the effect of the pressure of acetylene on the thermal isomerization of norbornadiene into cycloheptatriene. It was then shown that a pressure of acetylene reduces the breakdown of norbornadiene into acetylene and cyclopentadiene, and as a result we succeeded in raising the yield of cycloheptatriene obtained by the thermal isomerization of norbornadiene to 53.5% on the amount of the norbornadiene that reacted.

Cycloheptatriene was prepared first by Ladenburg in 1881 [7] and later by Merling in 1891 [8] from the alkaloids tropine and tropidine. Ladenburg called it tropyliene. In 1901 Willstätter [9] carried out a multistage synthesis of (II) from cycloheptanone, and until recently this classical method remained the only method for the preparation of cycloheptatriene [10], which made this substance almost inaccessible. From 1950 onward, however, several new and much simpler methods of preparing (II) were published: photosynthesis from benzene and diazomethane [11], solvolysis of bicyclo(3,2,0)hept-2-en-6-ol methanesulfonate, which was itself prepared from the product of the reaction of cyclopentadiene with ketene [12], pyrolysis of 7,7-dichloronorbornane, which was synthesized by reaction between cyclohexene and dichlorocarbene [13], and, finally, thermal isomerization of 2,5-norbornadiene [3-6]. We consider that the two methods described in this paper, namely the single-stage preparation of cycloheptatriene from cyclopentadiene and acetylene and the thermal isomerization of norbornadiene under a pressure of acetylene, are the most convenient and promising and that they make cycloheptatriene, which has some interesting properties, fairly accessible.

The condensation of acetylene with cyclopentadiene with the object of obtaining cycloheptatriene was carried out in the flow apparatus in which an optimum yield of norbornadiene was reached at about 350°, this yield being the greater the higher the pressure of acetylene, which we varied from 5 to 20 atm [2]. In the present work the condensation of cyclopentadiene with acetylene was studied at a higher temperature (390-415°) and at 5-7 atm. The dependence of the yields of cycloheptatriene and norbornadiene on temperature and pressure is shown in Fig. 1 and Table 1. It follows from these data that with rise in temperature the yield of cycloheptatriene rises and that of norbornadiene falls. Thus, at 5 atm a rise in reaction temperature from 400° to 410° led to doubling of the yield of cycloheptatriene (from 8.2% to 16.5%). At 7 atm with rise in temperature from 390° to 400° the yield of cycloheptatriene rose more than twofold (from 8.3% to 19.2%), i.e., at 7 atm a satisfactory result is attained at a lower temperature than at 5 atm.

TABLE 1. Results of Experiments on the Condensation of Cyclopentadiene with Acetylene in a Flow Apparatus

Temp. °C	Pressure (atm)	Rate		Yield (%)				
		of feed of cyclopentadiene (ml/hr)	of gas formed (liters/hr)	cyclopentadiene and its dimer	norbornadiene	toluene	cycloheptatriene	hexahydrodimethanonaphthalene
389	5,0	10,0	2,5	39,7	26,5	2,2	5,7	3,9
399	5,1	10,6	3,8	40,9	26,0	2,0	8,2	4,0
410	5,2	10,4	2,6	30,6	20,8	2,2	16,5	3,1
415	5,1	10,6	—	31,9	19,0	3,2	17,3	3,4
390	7,1	11,0	3,6	30,4	32,4	2,8	8,3	2,7
400	7,2	11,2	3,6	19,2	28,4	2,8	19,2	3,8
405	7,2	10,9	3,2	19,4	23,0	3,4	20,9	3,3
390	5,8	25,0	1,7	69,1	6,9	2,0	1,0	0,6
400	6,5	21,2	1,5	41,6	22,4	2,3	8,9	3,6
410	6,2	23,4	1,7	37,6	10,1	5,8	13,0	2,4
390	6,1	11,0	2,9	40,5	28,0	1,4	10,9	5,5
400	6,0	11,2	3,2	35,8	23,2	2,3	15,3	3,0
400	6,0	11,0	2,8	23,5	21,1	3,5	17,2	2,0
405	6,1	10,3	2,7	24,5	19,9	2,8	18,3	4,5
410	6,0	12,0	2,4	27,6	18,4	4,1	21,9	2,7

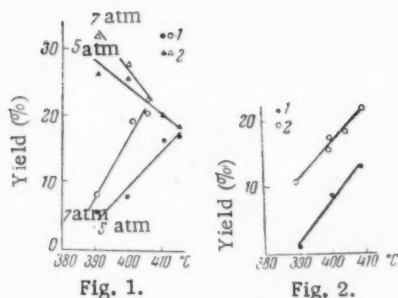
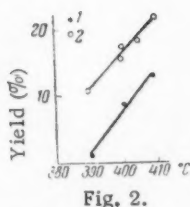


Fig. 1. Dependence of yields of cycloheptatriene (1) and 2,5-norbornadiene (2) on temperature at 5 and 7 atm with rate of feed of cyclopentadiene of 10-11 ml/hr. Fig. 2. Relation of yield of cycloheptatriene to temperature and rate of feed of cyclopentadiene: 1) 21-23 ml/hr; 2) 11-12 ml/hr.



The effect of the rate of feed of cyclopentadiene is shown in Fig. 2. At 6 atm and 410° reduction in the rate of feed by a factor of about two (from 23 to 12 ml/hr) led to a rise in the yield of cycloheptatriene from 13% to 22%. It should be noted that at a higher rate of feed the cyclopentadiene does not react completely and the reaction products contain much cyclopentadiene and its dimer. Under the given conditions there are formed also traces of benzene, 2-4% of toluene (product of the further isomerization of norbornadiene), and 2-4% of hexahydrodimethanonaphthalene (III) (product of the further condensation of norbornadiene with another molecule of cyclopentadiene [14]). It was found also that some of the high-boiling intermediate fractions obtained in experiments carried out at 400-415° had a bright-blue color, possibly due to the presence of azulenes.

The norbornadiene formed together with cycloheptatriene can, as already stated, be subjected to thermal isomerization into cycloheptatriene. Under optimum conditions at 395 ± 5°, Woods [5] obtained 44.8% of cycloheptatriene from norbornadiene. The effect of acetylene pressure on the thermal isomerization of norbornadiene was studied in the flow apparatus in which we carried out the preparation

of norbornadiene and cycloheptatriene. For comparison, experiments were also carried out in a quartz tube in absence of acetylene. The results are given in Table 2 and Fig. 3. From a comparison of the results obtained in Expt. 1 and 8 on the thermal isomerization of norbornadiene it will be seen that, whereas at atmospheric pressure the amount of cyclopentadiene formed was 16.4% on the amount of norbornadiene passed and 22.9% on the amount that reacted, with rise in acetylene pressure to 7.2 atm with about the same contact time the amount of cyclopentadiene formed by the breakdown of norbornadiene fell to 2.9% on the amount of norbornadiene passed and 3.9% on the amount that reacted. Suppression of the breakdown of norbornadiene favored increase in the yield of cycloheptatriene, which rose from 34.6% to 53.6% on the norbornadiene that reacted. Attention must be drawn to the fact that the increase in the yield of cycloheptatriene is particularly notable when calculated not on the norbornadiene passed, but on the amount that reacted. Thus, in Expts. 11 and 12, which had about the same contact time, the yield of cycloheptatriene calculated on the amount of norbornadiene passed increased only from 35.6% to 38.8% (i.e., by 3.2%) on rise in pressure from atmospheric to 4.2 atm, but from 41.3% to 52.8% (i.e., by 11.5%) when calculated on the amount of norbornadiene that reacted. In this respect the greatest effect is shown by an increase in pressure from atmospheric to 4 atm (cf. Expts. 1, 8, 9, and 10). In general, it is doubtful whether an increase in pressure to above

TABLE 2. Results of Experiments on the Thermal Isomerization of 2,5-Norbornadiene at 397°

Expt.	Acetylene pressure (atm)	Rate of passage of norbornadiene (ml/min)	Contact time (sec)	Yield of reaction products (%)				Losses of norbornadiene in course of reaction (% by wt.)	Fractionation losses (% by wt.)	Yield of cycloheptatriene (% by wt. on norbornadiene that reacts)
				cyclopentadiene	Norbornadiene	toluene	cycloheptatriene	heavy residue*		
10	2.2	0.21	24	8.2	42.4	9.2	21.7	6.9	5.6	37.5
9	4.2	0.21	24	5.5	30.9	8.3	33.9	14.4	2.3	47.1
8	7.2	0.22	23	2.9	27.7	7.5	38.3	15.6	3.9	53.6
11	4.2	0.15	34	2.4	26.2	8.2	38.8	17.6	3.0	52.8
5**	4.0	0.20	22	3.5	50.5	6.2	23.1	6.5	2.6	44.6
7**	8.0	0.20	25	3.6	23.4	9.2	36.3	15.9	9.6	47.2
1***	Atmospheric	0.50	26	16.4	29.7	11.6	24.9	8.1	3.9	34.6
12***	"	0.61	34	15.2	13.8	10.2	35.6	13.0	-	41.3

*The "heavy residue" is understood as that part of the reaction products that boil above cycloheptatriene.

**Expt. 5 was carried out at 392°; Expt. 7 at 386°.

***Experiments 1 and 12 were carried out in quartz tubes, diameters 1.5 and 2.0 cm, respectively.

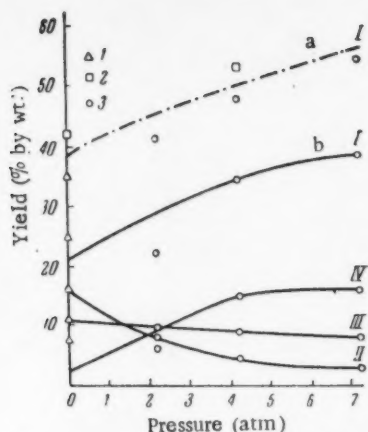


Fig. 3. Effect of acetylene pressure on yield of products of the thermal isomerization of 2,4-norbornadiene at 397° with a contact time of 1) 26.4 sec; 2) 34 sec; 3) 23-24 sec. I) Cycloheptatriene; a) on norbornadiene that reacted; b) on amount passed; II) cyclopentadiene; III) toluene; IV) heavy residue.

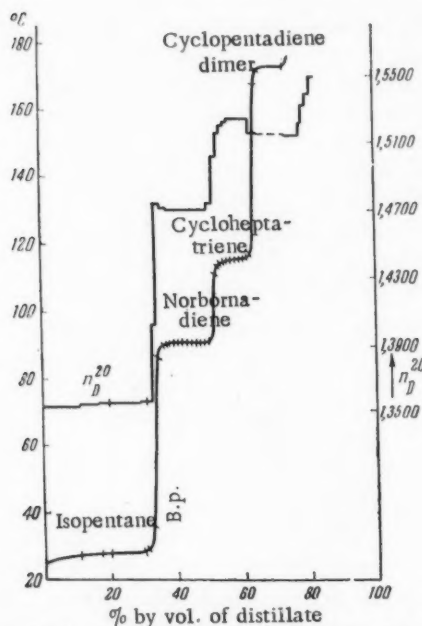


Fig. 5. Fractionation curve of products of the condensation of cyclopentadiene with acetylene at 400° and 6 atm. Boiling points adjusted to 760 mm.

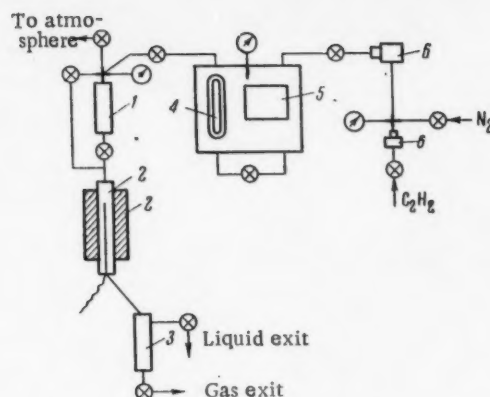


Fig. 4. Diagram of laboratory flow apparatus: 1) Dropping tube; 2) reactor with furnace; 3) separator; 4) differential manometer; 5) capillary [(4) and (5) form a rheometer for the gas feed]; 6) reversible valve.

8 atm is expedient, since the amount of high-boiling products formed increases with rise in pressure. As regards the yield of toluene, which appears to be a product of the further isomerization of cycloheptatriene, in the temperature range investigated pressure appears to have scarcely any effect.

An important factor influencing the yield of cycloheptatriene under the conditions studied is the time of contact; increase in contact time leads to increased yield of cycloheptatriene (cf. Expts. 5, 9, and 11, and also Expts. 1 and 12). As regards the effect of temperature, raising it by 11° (from 386° to 397°) led to an appreciable increase in the yield of cycloheptatriene (from 47.2% to 53.6%). At the temperature of the isomerization of norbornadiene resin formation is insignificant; in experiments under a pressure of acetylene the amount of resin formed did not exceed 0.1%, and in experiments at atmospheric pressure it was still less.

EXPERIMENTAL

The experiments were carried out in a laboratory flow apparatus (Fig. 4) constructed of 1Kh18N9T stainless steel. The volume of the reactor (diameter 22 mm) was 95 cc; the volume of the dropping tube was 115 cc. The temperature in the reactor was measured with a chromel-copel thermocouple, and the rate of feed of the liquid was regulated with a valve and checked by a drop counter. The apparatus was assembled in a steel safety box. Before and after the experiment, the apparatus was purged with nitrogen. In experiments on the condensation of acetylene with cyclopentadiene and on the thermal isomerization of norbornadiene the original liquid hydrocarbon was diluted with isopentane, which was taken in an amount of 87-120% by volume on the amount of hydrocarbon taken for reaction.

TABLE 3. Constants of Cycloheptatriene

B.p. in °C (p in mm)	M.p.(°C)	d_4^t	n_D^{20}	Literature reference
114	—	0,9129 (0°)	—	7
117 (749)	—	—	—	8
—	—	0,8876 (18,5°)	—	15
116	—	0,9083 (d_0^0)	$\left\{ \begin{array}{l} 1,52135 (n_{H\alpha}^{18,5^\circ}) \\ 1,54124 (n_{H\beta}^{18,5^\circ}) \\ 1,51751 (n_{H\gamma}^{17,5^\circ}) \\ 1,53688 (n_{H\delta}^{17,5^\circ}) \end{array} \right.$	9
115,50 (760)	-79,49	—	1,5243	10
115,55	-79,5	—	1,5213	16
114,5	—	—	—	11
60,5 (122)	—	—	1,5208 (25°)	12
116	—	—	1,5203—1,5209 (25°)	12
—	-75,24	—	—	17
116,3—117,0 (744)	—	—	1,5228	18
116—118 (760)	—	—	—	6
109—111 (630)	—	—	—	—
115,6	-75,1°	0,8915 (20°)	1,5244	Present work

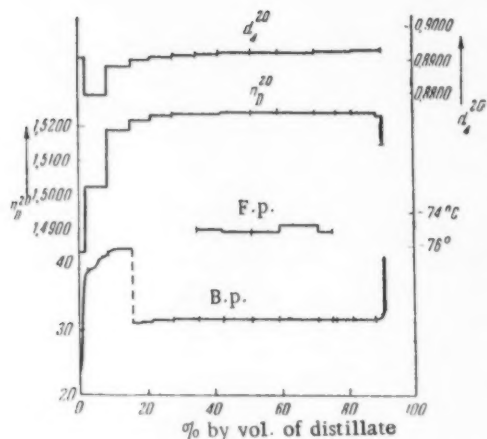


Fig. 6. Fractionation curve of cycloheptatriene.

The liquid reaction products were fractionated through a column of 15-plate efficiency having a glass filling. After the distillation at atmospheric pressure of isopentane and cyclopentadiene, when the temperature in the still was about 160°, fractionation was continued in a vacuum to avoid the depolymerization of cyclopentadiene dimer. The composition of the reaction products was determined from the fractionation curves, the compositions of narrow intermediate fractions being calculated on the basis of additivity of the refractive indices of the components. By way of example in Fig. 5, we give the fractionation curve of reaction products obtained in the condensation of cyclopentadiene with acetylene at 400° and 6 atm. Fractions containing cycloheptatriene from several experiments were combined and redistilled through a 50-plate column; 18% of the liquid was distilled off at 56 mm, and the remainder at 32 mm (Fig. 6).

The constants of pure cycloheptatriene as prepared by us are given in Table 3; in the same place we give all the values of constants given in the literature and from these it will be seen

that only Kohler and co-workers [10] had a relatively pure preparation, though, judging from the freezing point, it was not as pure as that described in the present paper. The purity of the cycloheptatriene prepared by us was found, in fact, to be 99.7 ± 0.1%, and the freezing point of absolutely pure cycloheptatriene calculated on the basis of our data is -74.8°. The cryoscopic constant for cycloheptatriene is 0.005 [19].

SUMMARY

1. An investigation was made of the condensation of acetylene with cyclopentadiene at high temperature with the object of preparing cycloheptatriene in one stage. At 400-405° with an acetylene pressure of 7 atm we obtained 20% of cycloheptatriene together with 20-25% of 2,5-norbornadiene.

2. A study was made of the effect of the pressure of acetylene on the thermal isomerization of 2,5-norbornadiene into cycloheptatriene, and it was shown that the use of acetylene under pressure diminishes the decomposition of 2,5-norbornadiene into cyclopentadiene and acetylene, as a result of which the yield of cycloheptatriene rises. Thus, at 397° increase in pressure from atmospheric to 7.2 atm led to an increase in the yield of cycloheptatriene from 34.8% to 53.5%, calculated on the amount of the norbornadiene that reacted.

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CHEMISTRY OF ACETALS

COMMUNICATION 3. REACTION OF THE BIS[DIETHYLACETALS]

OF MALONALDEHYDE AND METHYLMALONALDEHYDE

WITH ETHYL VINYL AND ETHYL PROPENYL ETHERS

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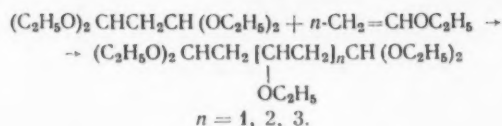
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 12, pp. 2184-2192, December, 1960

Original article submitted July 6, 1959

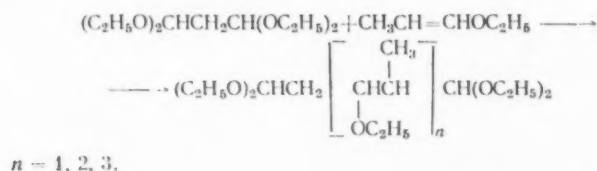
We previously [1] reported a simple general method for the synthesis of acetals of β -dicarboxyl compounds by the reaction of orthoformic ester with vinyl ethers, and by this method we prepared bis[diethyl acetals] of the malonaldehyde and acetoacetaldehyde series. It was considered to be of interest to study the possibility of further increase in length of the carbon chain, starting with these readily accessible compounds. In the first place we studied the reactions of the bis[diethyl acetals] of malonaldehyde and methylmalonaldehyde with ethyl vinyl and ethyl propenyl ethers. The reaction of malonaldehyde bis[diethyl acetal] with ethyl vinyl ether has been carried out previously by Protopopova and Skoldinov [2], who showed that in presence of boron trifluoride etherate reaction of the vinyl ether with a considerable excess of the acetal gave 1,1,3,5,5-pentaethoxypentane in 34% yield, calculated on the amount of vinyl ether taken.

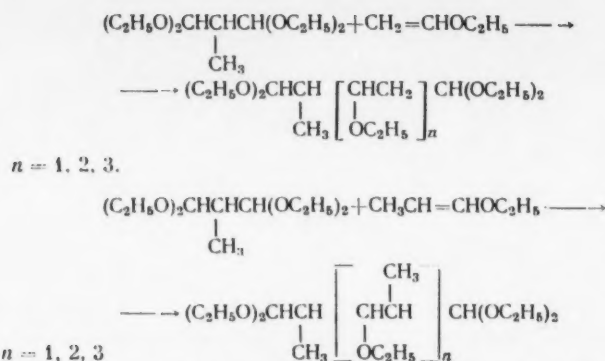
We studied the reaction between malonaldehyde bis[diethyl acetal] and ethyl vinyl ether in presence of zinc chloride. It was found that in this case reaction was sluggish and to bring it about it was necessary to heat the reaction mixture of 40-50°. Irrespective of the molar proportions of the reactants (we tried vinyl ether : acetal ratios of from 1 : 1 to 1 : 4), a mixture of the products of the addition of one, two, and three molecules of vinyl ether was always formed:



The proportions of primary, secondary, and tertiary products varied relatively little with change in the molar proportions of the reactants. Thus, the yield of the primary addition product 3-ethoxyglutaraldehyde bis[diethyl acetal] was 30% (on the acetal that reacted) when the ratio of reactants was 1 : 1, and 46% when the ratio was 1 : 4. The yield of the secondary addition product 1,1,3,5,7,7-hexaethoxyheptane increased from 12% to 20% on change in the ratio of reactants from 1 : 4 to 1 : 1, and the yield of the tertiary addition product 1,1,3,5,7,9,9-heptaethoxynonane increased from 10% to 15% for the same change in the ratio of reactants. The total yield of reaction products was therefore about 65-70%. As the optimum ratio of vinyl ether : acetal for the synthesis of the primary product we chose 1 : 2, at which the yield of primary product was usually 40-45%.

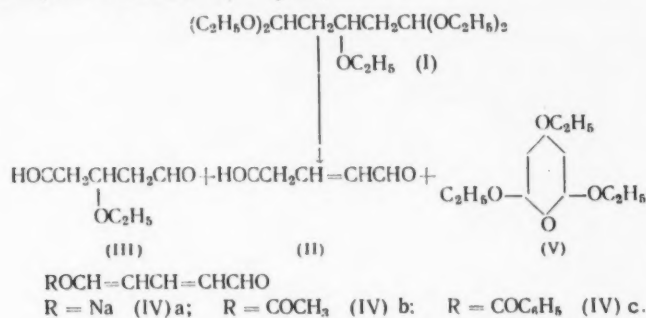
Apart from this reaction, which was carried out under conditions described in detail in the Experimental Part, we carried out the condensation of malonaldehyde bis[diethyl acetal] with ethyl propenyl ether and of methylmalonaldehyde bis[diethyl acetal] with ethyl vinyl and ethyl propenyl ethers; in the first two cases only the primary reaction products have been studied for the time being:



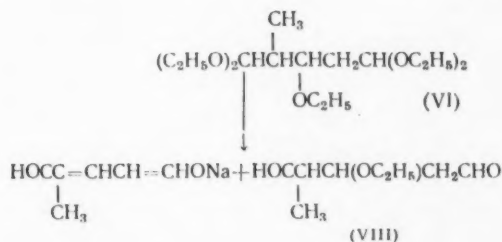


With the object of studying the properties of the bis[diethyl acetals] obtained, and also to confirm their structures, we investigated in the first place the hydrolysis of the bis[diethyl acetals] into the corresponding dialdehydes. It was found that all the bis[diethyl acetals] were extremely readily hydrolyzed, even by simple heating with distilled water in a water bath, with formation of the dialdehydes.

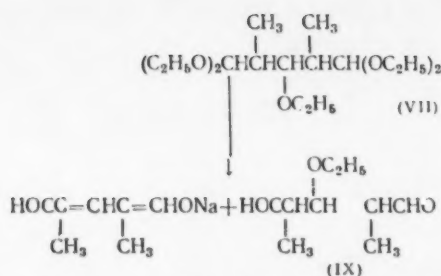
Under these conditions the hydrolysis of 3-ethoxyglutaraldehyde bis[diethyl acetal] (I) went in a complicated way and gave a mixture containing, according to the infrared spectrum,* glutaconaldehyde (II) (1687 cm^{-1}) and 3-ethoxyglutaraldehyde (III) (1718 cm^{-1}). On treatment of the mixture with sodium hydroxide it was possible to isolate the sodium salt of the enol form of glutaconaldehyde (IV a), which was characterized as the known acetate (IV b) and benzoate (IV c) [3]. After the separation of the sodium salt, from the neutral part we obtained a little 2,4,6-triethoxytetrahydropyran (V), the structure of which was confirmed by elementary analysis and the infrared spectrum (absence of absorption in the carbonyl region):



Analogous mild hydrolysis of the bis[diethyl acetals] of 3-ethoxy-2-methyl- (VI) and 3-ethoxy-2,4-dimethylglutaraldehydes gave high yields of the aldehydes themselves (VIII) and (IX). Together with these main products a small amount was obtained of the sodium salts of the enol forms of 2-methyl- and 2,4-dimethylglutaconaldehydes:



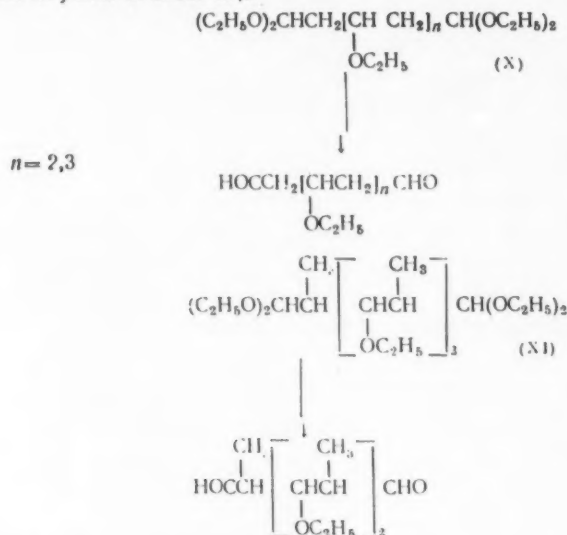
*The infrared spectra were determined by A. F. Vasil'ev.



The structures of the ethoxy dialdehydes (VIII) and (IX) were confirmed by their conversion respectively into 3-picoline and 3,5-lutidine by reaction with ammonium carbonate. Moreover, the infrared spectra of these dialdehydes contained characteristic absorption bands corresponding to an unconjugated aldehyde group (1718 cm^{-1}). The band at 1687 cm^{-1} , characteristic for a conjugated aldehyde group, was absent in both cases.

The structures of the enol forms of methyl- and dimethyl-glutaconaldehydes were confirmed by the ultraviolet spectra of their aqueous solutions examined in comparison with the ultraviolet spectrum of the known sodium salt of the enol form of glutaconaldehyde. In all cases there was an absorption maximum characteristic for a system of conjugated double bonds. It is interesting that in the ultraviolet spectra of the sodium salts of the enol forms of methyl- and dimethyl-glutaconaldehydes there are no bands characteristic for a conjugated aldehyde group, whereas in the ultraviolet spectrum of the sodium salt of the enol form of glutaconaldehyde such a maximum is present (at $226 \text{ m}\mu$). On treatment in alkaline aqueous solution with benzoyl chloride, the sodium salts of the enol forms of methyl- and dimethyl-glutaconaldehydes are converted into the corresponding crystalline benzoates, which correspond in analysis to the benzoates of the enol forms of these substituted glutaconaldehydes.

The hydrolysis of 1,1,3,5,7,7-hexaethoxyheptane (X; $n = 2$), 1,1,3,5,7,9,9-heptaethoxynonane (X; $n = 3$), and 1,1,3,5,7,7-hexaethoxy-2,4,6-trimethylheptane (XI) with water or very dilute (0.5%) phosphoric acid led to the corresponding ethoxy dialdehydes in yields of about 60%.



The structures of the ethoxy dialdehydes obtained were confirmed by analysis for ethoxyl content. However, these products were not completely pure, since the infrared spectra showed the presence of small amounts of products of the elimination of ethoxy groups (apart from the band at 1718 cm^{-1} there was a very weak band at 1687 cm^{-1}).

In continuation of the previous work we studied the reaction of orthoformic ester with some 1-substituted vinyl ethers (ethyl 1-ethylvinyl, ethyl 1-butylvinyl, and ethyl 1-phenylvinyl ethers) and 2-substituted vinyl ethers (1-butenyl ethyl and ethyl 1-octenyl ethers). The results then obtained confirmed the general laws of the reaction as established by us earlier [1]. As a result of the reaction we obtained the previously undescribed bis[diethyl acetals]

of 3-oxovaleraldehyde, 3-oxoheptanal,* and benzoylacetaldehyde, and also the bis[diethyl acetals] of ethyl- and pentyl-malonaldehydes. The structures of all the products were confirmed by their conversion into the corresponding 3(5)- or 4-substituted pyrazoles.

EXPERIMENTAL

Reaction of malonaldehyde bis[diethyl acetal] with ethyl vinyl ether. A solution of 43.2 g of ethyl vinyl ether in 50 g of malonaldehyde bis[diethyl acetal] was added over a period of four hours to a mixture of 181 g of the bis[diethyl acetal] and 30 g of saturated ethereal zinc chloride at 55-60°. The mixture was stirred for one hour at the same temperature and then treated with 20% sodium hydroxide solution; the organic layer was separated and dried (magnesium sulfate). Volatile substances were distilled off at the water pump, and the residue was fractionated through a 50-cm column with a full-condensation still ahead. We isolated the following:

- 1) 149.5 g of the original acetal; b.p. 77-80° (3 mm); n_D^{19} 1.4115;
- 2) 49.2 g (45.5% on the acetal that reacted) of 3-ethoxyglutaraldehyde bis[diethyl acetal]; b.p. 120-122° (3 mm); n_D^{19} 1.4220. Found: C 61.04; 61.23; H 10.80; 10.70%. $C_{15}H_{32}O_5$. Calculated: C 61.61; H 11.03%.
- 3) 13.5 g of 1,1,3,5,7,7-hexaethoxyheptane; b.p. 145-148° (3 mm); n_D^{22} 1.4295. Found: C 62.80; 63.00; H 10.90; 10.92%. $C_{19}H_{40}O_6$. Calculated: C 62.60; H 11.06.
- 4) 12.5 g of 1,1,3,5,7,9,9-heptaethoxynonane; b.p. 174-175° (2 mm); n_D^{22} 1.4350. Found: C 63.62; 63.47; H 10.84; 10.80%. $C_{23}H_{48}O_7$. Calculated: C 63.27; H 11.08%.

Reaction of malonaldehyde bis[diethyl acetal] with ethyl propenyl ether. A solution of 17.2 g (0.2 mole) of ethyl propenyl ether in 44 g (0.2 mole) of malonaldehyde bis[diethyl acetal] was added over a period of three hours to a mixture of 44 g (0.2 mole) of the bis[diethyl acetal] and 7.5 ml of a saturated ethereal solution of zinc chloride at 20-22°. The mixture was stirred at 50-60° for four hours. After the usual treatment and vacuum fractionation we isolated:

- 1) 65.3 g of the original acetal; b.p. 78-80° (2 mm); n_D^{19} 1.4145;
- 2) 15.7 g (43% on the acetal that reacted) of 3-ethoxy-2-methylglutaraldehyde bis[diethyl acetal]; b.p. 112-115° (2 mm); n_D^{19} 1.4251. Found: C 62, 53; 62.61; H 11.14; 11.08%. $C_{16}H_{34}O_5$. Calculated: C 62.71; H 11.32%.
- 3) 8.4 g of a fraction of b.p. 137-142° (1 mm); n_D^{19} 1.4335.
- 4) 3.9 g of a fraction of b.p. up to 187° (1 mm); n_D^{19} 1.4365. The substances (3) and (4) were higher addition products whose structures we have not yet studied.

Reaction of methylmalonaldehyde bis[diethyl acetal] with ethyl vinyl ether. A solution of 7.2 g (0.1 mole) of ethyl vinyl ether in 43.4 g (0.1 mole) of methylmalonaldehyde bis[diethyl acetal] was added over a period of 2.5 hr to a mixture of 43.4 g (0.1 mole) of the bis[diethyl acetal] and 5 ml of a saturated ethereal solution of zinc chloride. The reaction went with a moderate exothermic effect, and toward the end of the addition of the vinyl ether the rise of temperature reached a maximum of 28°; the mixture was then stirred for one hour at 50°. After the usual treatment and distillation of the reaction product through a 30-cm column with a full-condensation still head we obtained:

- 1) 27.6 g of the original acetal; b.p. 83-85° (3 mm); n_D^{20-5} 1.4145.
- 2) 11.6 g (46.2% on the acetal that reacted) of 3-ethoxy-2-methylglutaraldehyde; b.p. 124-127° (3 mm); n_D^{20} 1.4260. Found: C 62.60; 62.66; H 11.10; 11.10%. $C_{16}H_{34}O_5$. Calculated: C 62.71; H 11.32%.

In addition we obtained 6.3 g of a product of b.p. up to 180° (3 mm) and n_D^{20-5} 1.4310.

Reaction of methylmalonaldehyde bis[diethyl acetal] with ethyl propenyl ether. A solution of 17.2 g of ethyl propenyl ether in 46 g of methylmalonaldehyde bis[diethyl acetal] was added over a period of two hours to a mixture

*In the nomenclature of the original Russian this is named throughout as "butyrylacetaldehyde," which in the translator's nomenclature is "3-oxohexanal." However, the reactants stated will give "valerylacetaldehyde," i.e., 3-oxoheptanal, and this structure is in accord with the stated composition of the substance. The name "3-oxoheptanal" is given to this substance throughout.—Publisher.

of 47.6 g of the bis[diethyl acetal] and 7.5 ml of a saturated ethereal solution of zinc chloride at room temperature. The mixture was then stirred for two hours at 40-60°. On the next day, after the usual treatment and fractionation through a 30-cm column with a full-condensation still head, we obtained:

- 1) 64.9 g of the original acetal; b.p. 82-84° (3-4 mm); n_D^{20} 1.4145.
- 2) 16.4 g (42% on the acetal that reacted) of 3-ethoxy-2,4-dimethylglutaraldehyde; b.p. 133-136° (4 mm); 117-120° (2 mm); n_D^{20} 1.4298. Found: C 64.01; 64.17; H 11.01; 11.20%. $C_{17}H_{35}O_6$. Calculated: C 63.71; H 11.32%.
- 3) 9.8 g of 1,1,3,5,7,7-hexaethoxy-2,4,6-trimethylheptane; b.p. 162-165° (4 mm); 146-150° (2 mm); n_D^{19} 1.4405. Found: C 64.85; 64.72; H 11.11; 11.01%. $C_{22}H_{46}O_6$. Calculated: C 64.98; H 11.40%.
- 4) 1.8 g of a fraction of b.p. up to 195° and n_D^{20} 1.4425.

Hydrolysis of 3-ethoxyglutaraldehyde bis[diethyl acetal] (I) and reactions of the hydrolysis products. 1. A mixture of 26 g (0.089 mole) of 3-ethoxyglutaraldehyde bis[diethyl acetal], 10 ml of 1% phosphoric acid, and 30 ml of water was carefully stirred with heating in a water bath until a homogeneous solution was obtained. When cool, the light-brown solution was extracted twice with ether. The aqueous layer was made alkaline with 4 g of solid sodium hydroxide, and when the resulting brownish-red solution was cooled with ice there was a precipitate of the known sodium salt of the enol form of glutaconaldehyde in the form of beautiful golden-brown needles (1.6 g); λ_{max} (in water) 226 m μ (log ϵ 3.426); 363 m μ (log ϵ 4.545).

On shaking an alkaline aqueous solution of 2 g of the sodium salt of the enol form of glutaconaldehyde with 2 g of benzoyl chloride, we obtained 2.5 g of the benzoic ester of this enol compound, m.p. 119-121° (from aqueous alcohol) (the literature [3] gives m.p. 116-118°). Found: C 71.03; 71.17; H 4.90; 4.95%. $C_{12}H_{10}O_3$. Calculated: C 71.28; H 4.99%.

On treatment of the above-described salt with an equimolecular amount of acetic anhydride we obtained the acetic ester of the enol form of glutaconaldehyde, m.p. 73.5-75° (from petroleum ether) (the literature [3] gives m.p. 75°).

The ether extract obtained after the hydrolysis of the acetal (see above) was dried with magnesium sulfate; ether was distilled off, and the liquid residue was vacuum-distilled. Almost the whole of the product distilled in the range 80-82° (2 mm); n_D^{21} 1.4385. We obtained 7.8 g of liquid product, which analysis showed to be a mixture. To establish its composition we carried out the following reactions: a) on addition of a solution of 2 g of sodium hydroxide in 5 ml of water to 2.8 g of the liquid product there was a vigorous reaction and, on cooling, there was a precipitate of 0.9 g of the dihydrate of the sodium salt of the enol form of glutaconaldehyde, which gave a benzoate of m.p. 119-120°, identical with that described above. b) The liquid product (5 g) was mixed with ammonium carbonate (3 g), when heating and frothing of the mixture was observed. The liquid reaction products were distilled distilled off and dissolved in ether; the ethereal solution was dried (potassium hydroxide and magnesium sulfate). By careful fractionation we isolated 1.1 g of pyridine (b.p. 112-114° and n_D^{19} 1.5052), the picrate of which (m.p. 161-163.55°) was found to be identical with a known sample.

2. A mixture of 14.6 g (0.05 mole) of 3-ethoxyglutaraldehyde bis[diethyl acetal] and 20 ml of distilled water was stirred while being heated in a water bath until a homogeneous solution was formed. The resulting clear reddish-brown solution was mixed with a solution of 5 g (0.15 mole) of sodium hydroxide in 25 ml of water and cooled with ice. We isolated 5.3 g (68%) of the dihydrate of the sodium salt of the enol form of glutaconaldehyde, which gave its benzoic ester, identical with the sample described above.

The alkaline solution remaining after the isolation of the sodium salt was carefully extracted with ether, the extract was dried (magnesium sulfate), and after fractionation we obtained 1.5 g of 2,4,6-triethoxytetrahydropyran; b.p. 77-77.5° (1 mm); n_D^{20} 1.4352. Found: C 60.40; 60.70; H 9.95; 10.09%. $C_{11}H_{22}O_4$. Calculated: C 60.52; H 10.16%.

On treatment of 2,4,6-triethoxytetrahydropyran with 20% sodium hydroxide solution we obtained a yield of about 80% of the dihydrate of the sodium salt of the enol form of glutaconaldehyde, which on reaction in an alkaline medium with benzoyl chloride gave the benzoate of this enol compound, identical with the above, described sample.

3. A mixture of 14.6 g (0.05 mole) of 3-ethoxyglutaraldehyde bis[diethyl acetal] (I) and 20 ml of 5% phosphoric acid was stirred while being heated in a water bath until a homogeneous solution was formed. The mixture was cooled and made alkaline with a solution of 2.8 g of sodium hydroxide in 20 ml of water. To the cooled alkaline solution we added 8.5 g (0.05 mole) of benzoyl chloride with vigorous shaking. We obtained 7.4 g (70%) of the benzoic ester of the enol form of glutaconaldehyde, which after crystallization from benzene had m.p. 119.5-121°, undepressed by the sample described above.

Hydrolysis of 3-ethoxy-2-methylglutaraldehyde bis[diethyl acetal]. 1) A mixture of 17.7 g of 3-ethoxy-2-methylglutaraldehyde bis[diethyl acetal] and 20 ml of 1% phosphoric acid was stirred vigorously and heated in a water bath until a homogeneous solution was formed. The mixture was cooled and extracted with ether. The aqueous layer was made alkaline with 2 g of sodium hydroxide. Cooling gave a precipitate of the sodium salt of the enol form of methylglutaconaldehyde (0.6 g), which formed white silky needles, λ_{\max} (in water) 363 m μ (log ϵ 2.769).

In a manner similar to that described above we prepared the benzoic ester of the enol form of methylglutaconaldehyde from the sodium salt; slightly brownish needles, m.p. 110-112° (from alcohol). Found: C 72.32; 72.17; H 5.16; 5.21%. $C_{13}H_{12}O_3$. Calculated: C 72.21; H 5.59%.

The main ether extract (see above) was dried with magnesium sulfate and vacuum-fractionated. We obtained 7 g (62%) of 3-ethoxy-2-methylglutaraldehyde; b.p. 88-90° (2 mm); n_D^{20} 1.4395. Found: C 61.10; 60.98; H 9.29; 9.32%. $C_8H_{14}O_3$. Calculated: C 60.74; H 8.92%.

For proof of structure, 5 g of 3-ethoxy-2-methylglutaraldehyde was treated with 3 g of ammonium carbonate, as described above for the liquid product isolated after the hydrolysis of 3-ethoxyglutaraldehyde bis[diethyl acetal]. We obtained 1.3 g of 3-picoline, b.p. 142-145° and n_D^{15} 1.5085, the picrate of which had m.p. 148-149°, undepressed by admixture of a known sample.

2) A mixture of 5.4 g of 3-ethoxy-2-methylglutaraldehyde and 10 ml of 1% phosphoric acid was stirred and heated in a water bath until a dark-colored resin began to be precipitated. The solution was decanted from the resinous mass formed; it was cooled with ice, and 2 g of sodium hydroxide was added. The dark-colored mixture formed was diluted with acetone, and on the next day the precipitated sodium salt was separated. It was washed with acetone and ether and dried; this gave 4 g of sodium salt, from which by the usual method we obtained 1.5 g of the benzoic ester, identical with the above-described sample.

Hydrolysis of 3-ethoxy-2,4-dimethylglutaraldehyde bis[diethyl acetal] A mixture of 3-ethoxy-2,4-dimethylglutaraldehyde bis[diethyl acetal] (16.5 g) and 1% phosphoric acid (20 ml) was stirred and heated in a water bath for one hour. After being cooled, the mixture was treated in the usual way. From the aqueous layer we isolated a white crystalline precipitate of the sodium salt of the enol form of 2,4-dimethylglutaconaldehyde (0.8 g); λ_{\max} (in water) 275 m μ (log ϵ 2.051). From 0.6 g of the salt in the usual way we obtained 0.5 g of a crystalline benzoic ester m.p. 113-115.5° (from water). Found: C 73.50; 73.50; H 6.07; 5.80%. $C_{14}H_{14}O_3$. Calculated: C 73.02; H 6.13%.

From the ether extract after distillation we isolated 7 g (about 80%) of 3-ethoxy-2,4-dimethylglutaraldehyde; b.p. 101-104° (3 mm); n_D^{20} 1.4390. Found: C 62.85; 62.38; H 9.67; 9.77%. $C_9H_{16}O_3$. Calculated: C 62.76; H 9.36%.

From 2.6 g of the dialdehyde obtained and 3 g of ammonium carbonate in a similar way to that described above for the case of 3-ethoxy-2-methylglutaraldehyde we obtained 0.5 g of a liquid having n_D^{20} 1.5062, from which we prepared a picrate of m.p. 240-242° (from water), which corresponds to the melting point of 3,5-lutidine picrate [4]. Found: C 46.21; 46.50; H 3.60; 3.67%. $C_{13}H_{12}N_4O_7$. Calculated: C 46.03; H 3.60%.

Hydrolysis of 1,1,3,5,7,7-Hexaethoxyheptane. 1,1,3,5,7,7-Hexaethoxyheptane (18.2 g; 0.05 mole) was hydrolyzed with water (20 ml) in the usual way. The resulting homogeneous solution was extracted with ether. The extract was dried with magnesium sulfate, and fractionation gave 6.5 g (60%) of 3,5-diethoxyheptanediol; b.p. 100.5-102° (0.3-0.5 mm); n_D^{20} 1.4462. Found: C 60.72; 60.65; H 9.31; 9.39; OC_2H_5 40.34, 40.72%. $C_{10}H_{20}O_4$. Calculated: C 61.09; H 9.32; OC_2H_5 44.12%.

Hydrolysis of 1,1,3,5,7,9,9-heptaethoxynonane. The hydrolysis procedure was similar. From 10.9 g of 1,1,3,5,7,9,9-heptaethoxynonane we obtained about 3 g of 3,5,7-triethoxynonanediol; b.p. 140-145° (in the bath) at 0.5 mm; n_D^{20} 1.4510. Found: OC_2H_5 44.57; 45.02%. $C_{15}H_{28}O_5$. Calculated: OC_2H_5 46.87%.

The results of the carbon and hydrogen determinations were low (by 0.7-0.8% for C and 0.5-0.6% for H). The product was therefore not sufficiently pure. The low results are most readily explained by the high oxidizability of the dialdehyde, which rapidly acquires a yellow color when kept.

Hydrolysis of 1,1,3,5,7,7-hexaethoxy-2,4,6-trimethylheptane. The hydrolysis of 13.3 g of 1,1,3,5,7,7-hexaethoxy-2,4,6-trimethylheptane was carried out by heating it in a water bath with 15 ml of 1% phosphoric acid for 2.5 hr. After the usual treatment and two distillations we obtained 2.5 g of 3,5-diethoxy-2,4,6-trimethylheptane-dial; b.p. 112-115° (2 mm); n_D^{18} 1.4580. We did not succeed in isolating the dialdehyde in an analytically pure state; as in the preceding case, the results of carbon and hydrogen determinations were low, probably because of the high oxidizability of the dialdehyde. Found: OC_2H_5 36.06; 36.81%. $\text{C}_{12}\text{H}_{24}\text{O}_4$. Calculated: OC_2H_5 38.78%.

Preparation of benzoylactaldehyde bis[diethyl acetal]. Slowly, at not above 30-35°, 14.8 g (0.1 mole) of ethyl 1-phenylvinyl ether was added to 29.6 g (0.2 mole) of orthoformic ester and 10 ml of a saturated ethereal solution of zinc chloride; the mixture was stirred for one hour at 40-45° and then treated with 20% sodium hydroxide solution. The organic layer was separated, dried (magnesium sulfate), and vacuum-fractionated. We obtained 19.5 g (65%) of benzoylactaldehyde bis[diethyl acetal], b.p. 148-150° (8 mm) and n_D^{22} 1.4692; on standing it crystallized. Found: C 68.89; 68.70; H 9.38; 9.38%. $\text{C}_{17}\text{H}_{28}\text{O}_4$. Calculated: C 69.89; H 9.52%.

For confirmation of the structure, 16.3 g of the bis[diethyl acetal] was added to a solution of 3.7 g of hydrazine hydrochloride and 2.5 ml of 2 N HCl in 10 ml of water at 45-50°. The mixture was heated for one hour at this temperature and then for 10-15 min in a boiling water bath. The clear solution was cooled and treated with 50 ml of 40% sodium hydroxide solution; the mixture was extracted with ether, and the extract was dried with magnesium sulfate. Distillation gave 5.2 g (69%) of 3(5)-phenylpyrazole, b.p. 155-157° (3 mm), which solidified. After crystallization from water the crystals had m.p. 76.5-79°, which is in accord with data in the literature [5]. Found: N 19.19; 19.24%. $\text{C}_9\text{H}_8\text{N}_2$. Calculated: N 19.43%.

The picrate prepared from the phenylpyrazole had m.p. 172-172.5°, which is in accord with the literature [5].

Preparation of 3-oxoheptanal bis[diethyl acetal]. Proceeding as in the preceding case, from 12.8 g (0.1 mole) of 1-butylvinyl ethyl ether and 29.6 g of orthoformic ester we obtained 15.6 g (56%) of 3-oxoheptanal bis[diethyl acetal]; b.p. 120-122° (9 mm); n_D^{22} 1.4260. Found: C 65.37; 65.19; H 11.36; 11.26%. $\text{C}_{15}\text{H}_{32}\text{O}_4$. Calculated: C 65.18; H 11.67%.

Proceeding as in the preceding case, from 11.7 g of the bis[diethyl acetal] we obtained 2.7 g (50%) of 3(5)-butylpyrazole, b.p. 115-117° (6 mm) and $n_D^{19.5}$ 1.4830, the picrate of which had m.p. 110.5-111.5° (from benzene). Found: N 20.45; 20.25%. $\text{C}_{13}\text{H}_{15}\text{O}_6\text{N}_5$. Calculated: N 20.76%.

Preparation of 3-Oxovaleraldehyde bis[diethyl acetal]. Analogously, from 20 g (0.2 mole) of ethyl 1-ethylvinyl ether and 59.2 g (0.4 mole) of orthoformic ester we obtained 29.1 g (60%) of 3-oxovaleraldehyde bis[diethyl acetal]; b.p. 71-73° (1 mm); $n_D^{17.5}$ 1.4222. Found: C 62.65; 62.74; H 11.12; 11.10%. $\text{C}_{13}\text{H}_{28}\text{O}_4$. Calculated: C 62.87; H 11.37%.

By the above-described method, from 12.4 g of the bis[diethyl acetal] we obtained 2 g (40%) of 3(5)-ethylpyrazole, b.p. 95-96° (7 mm) and n_D^{20} 1.4918, the picrate of which had m.p. 129.5-130.5° (from benzene), which is in accord with the literature [6].

Preparation of ethylmalonaldehyde bis[diethyl acetal]. Analogously, from 13.7 g (0.137 mole) of 1-butenyl ethyl ether and 29.6 g (0.2 mole) of orthoformic ester in presence of 5 ml of a saturated ethereal solution of zinc chloride we obtained 23.2 g (69%) of ethylmalonaldehyde bis[diethyl acetal]; b.p. 116-118° (16 mm); n_D^{20} 1.4190. Found: C 62.88; 63.02; H 11.41; 11.40%. $\text{C}_{13}\text{H}_{28}\text{O}_4$. Calculated: C 62.87; H 11.37%.

In the usual way, from 4.8 g of the bis[diethyl acetal] we obtained 1.5 g of 4-ethylpyrazole, b.p. 87-89° (2 mm) and n_D^{20} 1.4868, the picrate of which had m.p. 142-145.5° (from benzene). Found: N 21.21; 21.23%. $\text{C}_{11}\text{H}_{11}\text{N}_5$. Calculated: N 21.53%.

Preparation of pentylmalonaldehyde bis[diethyl acetal]. In the usual way, from 14.2 g (0.1 mole) of ethyl 1-octenyl ether and 22.2 g (0.15 mole) of orthoformic ester we obtained 18.8 g (65%) of pentylmalonaldehyde bis[diethyl acetal]; b.p. 143-146° (15 mm); n_D^{19} 1.4252. Found: C 66.05; 66.03; H 11.66; 11.67%. $\text{C}_{16}\text{H}_{34}\text{O}_4$. Calculated: C 66.16; H 11.80%.

In the usual way, with the exception that 15 ml of 1 : 1 hydrochloric acid was used, from 14.5 g of the bis[diethyl acetal] we obtained 1.4 g of 4-pentylpyrazole, b.p. 118-120° (2 mm) and $n_D^{16.5}$ 1.4792, the picrate of which had m.p. 75.5-77.5° (from benzene). Found: N 16.63; 16.70%. $C_{14}H_{17}O_7N_5$. Calculated: N 16.80%.

SUMMARY

1. A study was made of the possibility of using the bis[diethyl acetals] of malonaldehyde and methylmalonaldehyde in chain-lengthening reactions with ethyl vinyl and ethyl propenyl ethers.

2. A method was developed for the preparation of the bis[diethyl acetals] of 3-ethoxyglutaraldehyde, 3-ethoxy-2-methylglutaraldehyde, and 3-ethoxy-2,4-dimethylglutaraldehyde, and the hydrolysis of these acetals was studied.

3. The bis[diethyl acetals] of 3-oxovaleraldehyde, 3-oxoheptanal, benzoylactaldehyde, ethylmalonaldehyde, and pentylmalonaldehyde were prepared for the first time.

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LAWS AND MECHANISM OF THE CYCLIZATION OF ISOPRENOIDS *

COMMUNICATION 2. ** CYCLIZATION OF *cis*- AND *trans*-GERANYLACETONES

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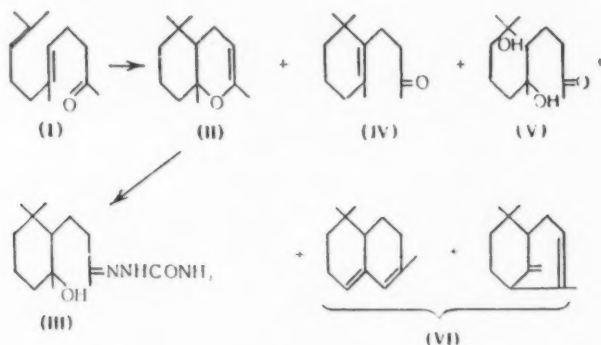
No. 12, pp. 2193-2200, December, 1960

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Numerous investigations devoted to the study of the biosynthesis of triterpenes and steroids have made it possible to formulate a biogenetic rule for isoprenoids [2] in accordance with which it was found possible to give a unified scheme for the formation in nature of polycyclic terpenes and steroids by the structurally selective and stereospecific cyclization of their acyclic precursors. This transformation, which in the living organism proceeds under the action of enzymes, may be modeled by the cyclization of isoprenoids under the action of acid catalysts, a reaction that has been studied widely in recent years [3]. The possibility of carrying out this reaction in a stereospecific manner was demonstrated in a number of simple cases [4-7], but the method proposed for this is convenient only for the cyclization of acids.

We set ourselves the task of working out a more general method for the structurally and sterically selective cyclization of isoprenoids. We showed earlier [1] that the method of low-temperature cyclization in nitro paraffin solution under the action of 100% sulfuric acid is fairly convenient for the cyclization of ketones of the type of pseudoionone and makes it possible to reduce the extent of the isomerization of the primary cyclization products to a minimum. In the present work it was shown that the same method makes it possible to effect the smooth cyclization of ketones of the type of geranylacetone [6,10-dimethyl-5,9-undecadien-2-one] and to study the structural and steric orientation in this reaction.

No convenient methods of cyclization have been reported in the literature for ketones of this type, and therefore in the first place we made a detailed investigation of the possibility of using various agents for this reaction. As shown earlier by Naves [8], under the action of BF_3 geranylacetone (I) gives a complex mixture of products, from which in a yield of only about 17% was isolated 4a,5,6,7,8,8a-hexahydro-2,5,5,8a-tetramethyl-4H-1-benzopyran (II), which readily gave a hydroxy tetrahydroionone derivative (III) and was isomerized under the action of acids into dihydro- β -ionone (IV). We found that in the cyclization of (I) with the aid of the usual cyclizing agents the following mixture of reaction products may be formed:



*The present investigation was begun under the direction of Academician I. N. Nazarov.

**For Communication I see [1].

TABLE 1

Amt. of cyclizing agent [g per 10 g of (I)]	Amt. of solvent [ml per 10 g of (I)]	Temp. (°C)	Time (min)	Total yield of cyclization products (%)	C=O content of mixture (%)	Yield (%)		
						(II)	(IV)	(V)
H ₂ SO ₄ (98%), 50 g	Ether 40	-5	80	65	72	15	—	10
H ₃ PO ₄ (85%), 50 g	Ether 50	60	60	60	15	—	—	—
(H ₃ PO ₄) _x , 15 g	—	30	10	35	7	—	—	—
HCOOH, 30 g + H ₂ SO ₄ 4,0 g	—	5	40	70	65	15	—	—
HCOOH, 30 g	—	70	40	80	70	—	25	—
BF ₃ (C ₂ H ₅) ₂ O, 10 g	Benzene 80	50	30	65	40	—	10	—
BF ₃ ·H ₃ PO ₄ , 20 g	—	-30—50	15	53	92	20	—	40*
BF ₃ ·H ₃ PO ₄ , 20 g	—	-30—50	15	40	91	20	—	—**
Kationit KU-2, 10 g	Water 1 ml	95	60	70	10	—	5	—
HClO ₄ (73%) 17,0 g	—	-28—35	20	43	85	30	—	50
The same	—	30	2	36	85	25	—	45
"	CH ₃ NO ₂ , 20 ml	-60	30	50	96	40	—	30
"	(CH ₃ CO) ₂ O, 55 g	25	4	65	80	50	—	5
HClO ₄ (73%), 17 g + P ₂ O ₅ , 12,5 g	—	4—8	5	60	90	45	—	20
the same	Ether 10 ml	-10	3	65	90	55	—	15

*The mixture was decomposed with water.

**The mixture was decomposed with pyridine; 40% of (I) was regenerated.

TABLE 2

Amt. of cyclizing agent [g per 10 g of (I)]	Amt. of solvent [ml per 10 g of (I)]	Temp. °C	Time (min)	Total yield of cyclization products (%)	C=O content of mixture (%)	Yield (%)		
						(II)	(IV)	(V)
100% H ₂ SO ₄ 27 g	C ₃ H ₇ NO ₂ , 20	-65	20	80	95	72	—	—
The same	C ₃ H ₇ NO ₂ , 20	-90	15	82	88	60	—	—
"	CH ₃ NO ₂ , 20	-55	35	84	95	65	—	5—10
100% H ₂ SO ₄ , 1.7 g	CH ₃ NO ₂ , 20	-30	65	—	—	—	—	*
100% H ₂ SO ₄ , 34 g	Ether 20	-30	10	85	75	55—60	—	10
Oleum, 15%, 34 g	Ether 20	-30	10	50	85	40	—	—
77%, 18.0 g	—	-25	5	55	72	20	—	40
64%, 30 g	—	10	20	50	60	—	5	40

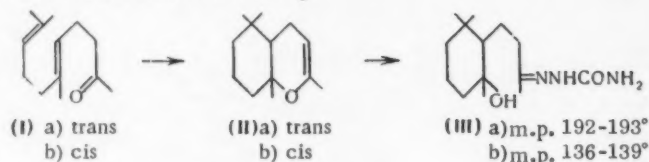
* (I) was completely regenerated.

The analysis of the mixture formed was carried out as follows: the hydration product 6,10-dihydroxy-6,10-dimethyl-2-undecanone (V) was readily separated because of its good solubility in water; in the remaining mixture the total content of (II) and (IV) was determined by oxime formation, and the individual products were isolated as semicarbazones. The hydrocarbon fraction was not investigated in detail, and its possible structure was based on Stoll's data [9]. Our results on the cyclization of (I) under the action of various agents are given in Table 1. It will be seen that the contents of the reaction products in the mixture depend both on the nature of the cyclizing agent and on the reaction conditions. The formation of (V) depends on the water content of the reaction mixture, and the amount of (VI) and (IV) is determined mainly by the reaction temperature and may be reduced to a minimum only at low temperatures. It was just for this reason that the classical methods of carrying out the reaction of cyclization (0-30°, nonabsolute media) were found to be quite unsuitable for the structurally unequivocal cyclization of (I). The use of various acid catalysts under these conditions did not lead to satisfactory yields of the benzopyran derivative (II). A more suitable agent was found in the complex BF₃·H₃PO₄, which permitted us to lower the reaction temperature, shorten the reaction time, and almost eliminate the formation of (IV) and (VI). The yield of the diol (V) was determined by the concentration of perchloric acid and did not depend on other factors (temperature, reaction time, amount of acid). We succeeded in suppressing the formation of (V) by reduction of the water content of the

reaction medium by the addition of P_2O_5 or $(CH_3CO)_2O$. In this way the yield of the benzopyran (II) was raised to 50-55%, but a mixture was then formed which was liable to explode

Further investigations on the choice of conditions showed that the benzopyran (II) could be obtained in good yield only by use of 100% sulfuric acid at low temperature in nitro paraffin solution (Table 2). Under these conditions the reaction proceeds in one way only and the yield of the benzopyran derivative may attain 70-75%. The replacement of nitro paraffins by other solvents of low freezing point gives worse results.

The convenient method of cyclizing geranylacetone that we had developed, which enabled us to carry out the reaction under the mildest conditions, made it possible for us to study steric orientation in this reaction, which was important for the confirmation of the general laws of the stereochemistry and mechanism of the cyclization of isoprenoids. For this purpose geranylacetone, prepared by Caroll's method [10] and consisting of a 3 : 2 mixture of trans and cis isomers, was resolved by fractionation through a column of 100-plate efficiency. The fractions obtained were purified through their semicarbazones, and as a result we isolated the individual stereoisomers of geranylacetone: trans-geranylacetone (Ia), semicarbazone m.p. 95-95.5° (the literature [11] gives m.p. 92-93°), and cis-geranylacetone (Ib), semicarbazone m.p. 89-90° (the literature [11] gives m.p. 90-91°). In the cyclization of (Ia) we obtained the benzopyran (IIa) in about 80% yield, and this gave a high yield of the semicarbazone of the hydroxy tetrahydroionone (IIIa), m.p. 192-193° (the literature [8] gives m.p. 193-193.5°). Under the same conditions the cyclization of (Ib) led to the isomeric benzopyran (IIb), which formed a semicarbazone of m.p. 136-139° (IIIb) (the literature gives: m.p. 137° [12]; m.p. 138-145° [13]). In the cyclization of the 3 : 2 mixture of (Ia) and (Ib) we obtained a mixture of the benzopyrans (IIa) and (IIb), from which we isolated 50% of (IIIa) and about 10% of (IIIb). As was proved by Ohloff [14], the benzopyran (IIa), which gives the semicarbazone (IIIa) of m.p. 192-193°, has the trans-fusion of the rings and therefore the isomeric benzopyran (IIb), which gives the semicarbazone (IIIb) of m.p. 136-139°, must have the cis-fusion of the rings.



The results show that under the conditions that we have worked out the cyclization of geranylacetone proceeds stereospecifically, and the trans-isomer (Ia) forms a benzopyran with a trans-fusion of the rings, while the cis-isomer (Ib) forms a benzopyran with a cis-fusion of the rings.* This result is in good accord with the views of Ruzicka on the mechanism of the cyclization of isoprenoids.

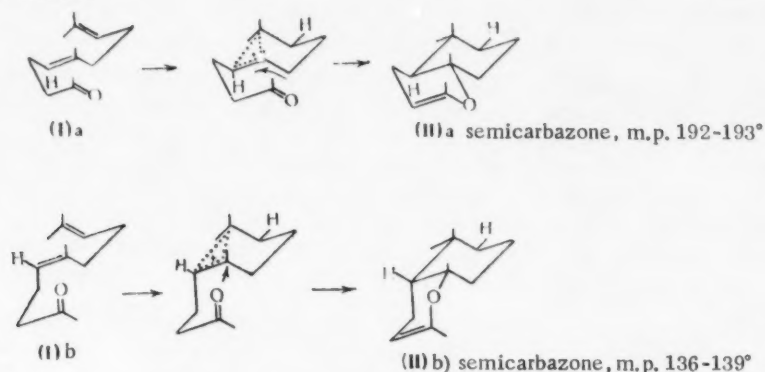
It follows from these views that two extreme cases of the mechanism of the cyclization of 1,5-dienes are possible, the cyclization being regarded as a special case of electrophilic addition at a $C = C$ bond. In the first case the reaction may proceed with intermediate formation of classical flat carbonium ions, while in the second it may proceed through the stage of the formation of a nonclassical cation in which the original configuration of the substituents is preserved. It is clear that, if in any of the configuration-determining stages of the reaction the intermediate product is a classical carbonium ion, then in general, a mixture of the possible stereoisomers must be formed with a predominance of the energetically more favored form. If, however, an intermediate phase of the reaction is a nonclassical cation or π -complex, then in this case the reaction must proceed by an antiparallel-addition scheme and give products whose configurations are determined only by the configuration and conformation of the original diene. It follows that in the formation of a bicyclic system as a result of the cyclization of an acyclic 1,5,9-triene, the stereochemistry of the ring fusion will be determined by the disposition of the substituents at the 5,6- $C = C$ bond only if the reaction goes in one stage without formation of stable intermediate monocyclic products.** If, however, the cyclization goes as a result of the successive closure first of one and then of the other ring, then the bicyclic product formed, irrespective of the isomerism at the $C = C$ bond in the original triene, should have cis-fusion of the rings, as occurs in the cyclization of butenylcyclohexenes [7].

*Naves [8] showed that, under the action of BF_3 , both from pure (Ia) and from a mixture of (Ia) and (Ib) one and the same trans-benzopyran (IIa) was formed in the same yield in each case.

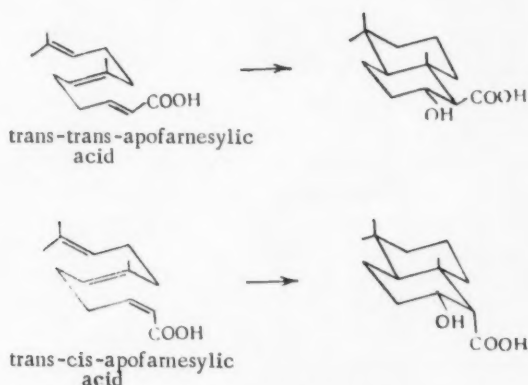
**For acyclic compounds only the energetically more favored chair conformation is considered.

The application of these concepts to our case of the stereospecific cyclization of geranylacetone enables us to present the mechanism of this reaction in the general form given below.

As the cyclization of (I) was found to be stereospecific, the formation of a flat carbonium ion is excluded in the configuration-determining phase of the reaction, i.e., the stage in which the ring is formed. The stereospecificity of the cyclization shows also that the formation of the bicyclic benzopyran does not pass through the intermediate stage of the closing of one ring first, as otherwise both from (Ia) and from (Ib) one and the same cis-benzopyran (IIb) should be formed.



Hence, our results show that in the formation of the benzopyran bicyclic system, both rings are closed simultaneously, and the bonds formed are antiparallel, as they should be if the formation of a nonclassical cation is regarded as an intermediate stage in the reaction. It must be mentioned that in very few investigations on the stereochemistry of the cyclization of acyclic compounds have only compounds with a *trans* configuration of the central C = C bond been investigated [6, 15], and this did not permit an unequivocal solution of the question of steric orientation of the reaction at this center, which determines the stereochemistry of the fusion of the rings. The question of steric orientation in the reaction has been resolved fairly strictly only for a terminal double bond [4, 5, 6], which moreover was disubstituted, as in the case of apofarnesyl acid [6], and not trisubstituted which is the most characteristic for isoprenoids. The results of our experiments on the stereospecific cyclization of geranylacetone show that, in those cases also in which reaction proceeds with participation of a trisubstituted C = C bond and the intermediate formation of an energetically favored tertiary carbonium ion is possible, the reaction nevertheless proceeds as antiparallel and simultaneous addition at the double bonds taking part in the reaction with the probable intermediate formation of a nonclassical cation (π -complex).



EXPERIMENTAL

Cyclization of trans-geranylacetone (Ia). A solution of 30 ml of 100% sulfuric acid in 40 ml of dry nitropropane was cooled to -65° , and with stirring 20 g of trans-geranylacetone was added over a period of 15 min. The clear lemon-yellow solution formed was kept for a further five minutes at this temperature, and then poured with

stirring into a mixture of 300 ml of petroleum ether and 400 ml of ice water. The colorless organic layer was separated, and the aqueous layer was extracted with four 100-ml portions of petroleum ether; the combined extracts were washed with sodium bicarbonate solution and water and were dried with potassium carbonate. After removal of solvent, the residue was vacuum-distilled. We obtained 16.0 g of the trans-benzopyran (IIa), b.p. 67-68° (1 mm) and n_D^{20} 1.4850 (the literature [8] gives: b.p. 82-83° (2 mm); n_D^{20} 1.4865); from oxime-formation data the cyclization product contained 95% of keto group.

From 3.0 g of (IIa) we obtained 3.7 g (90%) of the semicarbazone (IIIa) (m.p. 183-185°) in the usual way; after two crystallizations from aqueous methanol it had m.p. 192-193° (the literature [8] gives b.p. 193-193.5°). Found: C 62.02; 62.15; H 10.04; 9.84; N 15.54; 15.46%. $C_{14}H_{27}N_3O_2$. Calculated: C 62.42; H 10.00; N 15.6%.

Cyclization of cis-geranylacetone (Ib). By an analogous procedure to that of the preceding experiment, from 4.0 g of cis-geranylacetone we obtained 2.6 g of the cyclization product (IIb), b.p. 67-72° (1 mm) and n_D^{20} 1.4820, which according to oxime-formation data contained 92% of a keto group. From 2.2 g of this product we obtained 2.7 g of the semicarbazone as a thick oil, which gradually crystallized out (m.p. 100-125°). After crystallization from ethyl acetate we obtained 1.2 g of the semicarbazone (IIIb), m.p. 136-139° (the literature gives: m.p. 137° [13]; m.p. 138-145° [12]); from the mother liquor a further 0.3 g of (IIIb), m.p. 124-130°, we isolated. The residue remaining after the separation of (IIIb) was a noncrystallizing oil. The total yield of (IIIb) was 50% [calculated on the amount of (IIb)].* Found: C 62.48; 62.65; H 10.23; 10.09%; $C_{14}H_{27}N_3O_2$. Calculated: C 62.42; H 10.00%.

Cyclization of the 2 : 3 mixture of cis- and trans-geranylacetones. The original geranylacetone was prepared by Carroll's method [10] and had b.p. 74-78° (1 mm) and n_D^{20} 1.4670. The experiment was carried out similarly to those described above. From 20 g of the mixture of (Ia) and (Ib) we obtained 14.5 g of a mixture of (IIa) and (IIb), b.p. 61-66° (1 mm) and n_D^{20} 1.4840, containing 92% of a keto group according to oxime-formation data. From 3.0 g of this mixture we prepared in the usual way 2.5 g (50%) of the semicarbazone (IIIa), m.p. 183-185°, identical with the product described in the first experiment. From the mother liquor, after removal of solvent, we succeeded in isolating about 0.25 g of the semicarbazone (IIIb), m.p. 135-141° (yield about 6%).

Cyclization of geranylacetone under the action of 73% $HClO_4$.** Geranylacetone (10 g) was added to stirred perchloric acid (10 ml) cooled to -35° at such a rate that the temperature did not rise above -30° (5 min). The mixture was then kept for a further five minutes at this temperature and poured with stirring into a mixture of 100 ml of ether and 100 ml of ice water. The ether layer was separated, the aqueous solution was extracted with ether, and the combined extracts were washed with sodium bicarbonate solution and dried with potassium carbonate (Extract 1). The acid aqueous solution was neutralized with 40% NaOH and extracted with ether for 20 hr in a percolator (Extract 2).

After the removal of ether from Extract 1 there remained 4.3 g of a mixture of benzopyrans as a colorless liquid of n_D^{20} 1.4822 having a 90% content of ketone according to oxime-formation data and giving a 56% yield of the semicarbazone (IIIa), m.p. 192-193°. From Extract 2, after it had been dried with potassium carbonate,*** freed from ether, and vacuum-distilled, we obtained 5.5 g of the diol (V) as a viscous liquid, b.p. 153-155° (1 mm) and n_D^{20} 1.4726. Found: C 67.72; 67.90; H 11.31; 11.48%. $C_{13}H_{26}O_3$. Calculated: C 67.72; H 11.38%.

Proof of the structure of the diol (V). The diol (V) (13.0 g) was heated in a vacuum in presence of traces of $KHSO_4$. At 190° vigorous liberation of water began; it ceased after five minutes. The mixture was cooled and extracted with ether; the extract was dried and distilled. We obtained 8.9 g of a mixture of geranylacetone isomers, b.p. 97-105° (2 mm) and n_D^{20} 1.4648. For (I) the literature [8] gives b.p. 92-93° (2 mm) and n_D^{20} 1.4650. On hydrogenation of the product over platinum in ethanol 1.8 moles of hydrogen was absorbed and tetrahydrogeranyl acetone was formed, b.p. 87-89° (2 mm) and n_D^{25} 1.4375, from which an 85% yield was obtained of the semicarbazone, m.p. 93-94° (from aqueous methanol) (the literature [16] gives m.p. 95-96°), undepressed by admixture of a known sample.

*The relatively low yield of the semicarbazone (IIIb) is possibly to be explained by a slight admixture of difficultly soluble (IIIa).

**In all experiments on the choice of conditions the admixture of cis- and trans-geranylacetones was used. From the resulting mixture of (IIa) and (IIb) we isolated only the readily separable semicarbazone (IIIa), corresponding to (IIa).

***When Extract 2 was dried with acidic drying agents, in the subsequent distillation the dehydration of (V) sometimes occurred.

Cyclization of geranylacetone under the action of a mixture of HClO_4 and P_2O_5 . At -10° 12.5 g of phosphorus pentoxide was added gradually to 10 ml of perchloric acid (73%) with rise in temperature toward the end of the addition to $30-35^\circ$. The greenish solution obtained was filtered, diluted with 10 ml of dry ether, and cooled to -35° . Then, over a period of six minutes 10.0 g of geranylacetone was added to the stirred mixture in such a way that the temperature did not exceed -25° . Stirring was continued for ten minutes at -30° , and the mixture was poured into a mixture of 150 ml of ice water and 150 ml of ether. The further treatment was carried out as described for the preceding experiment. We isolated 6.6 g of a mixture of the benzopyrans (IIa) and (IIb) of n_D^{21} 1.4855 assaying 90% of keto group (oxime formation), and giving a 52% yield of the semicarbazone (IIIa), which had m.p. $192-193^\circ$ after recrystallization. From the acid aqueous solution we isolated 2.6 g of the diol (V), b.p. $160-161^\circ$ (2 mm) and n_D^{21} 1.4722.

Cyclization of geranylacetone under the action of the complex $\text{BF}_3 \cdot \text{H}_3\text{PO}_4$. a) Geranylacetone (10.0 g) was added with stirring to the complex $\text{BF}_3 \cdot \text{H}_3\text{PO}_4$ (20.0 g) cooled to -60° in such a way that the temperature did not rise above from -35° to -30° (15 min). The resulting orange viscous mass was decomposed by the addition of 50 ml of ice water. After the usual treatment we isolated 5.3 g of a mixture of the benzopyrans (IIa) and (IIb) of n_D^{16} 1.4825, which assayed at 92% of keto group (oxime formation) and gave the semicarbazone (IIIa), m.p. $192-193^\circ$ (from methanol), in 40% yield. From the acid aqueous solution we isolated 4.7 g of the diol (V), n_D^{20} 1.4710.

b) Under the same cyclization conditions, but with a preliminary treatment with pyridine before the decomposition with water, we obtained 9.3 g of reaction product, from which by distillation we isolated 3.9 g of substance corresponding in its constants to the benzopyran (n_D^{21} 1.4805, 91% of keto group), which gave a 45% yield of the semicarbazone, m.p. $192-193^\circ$, and 3.3 g of geranylacetone, b.p. $90-92^\circ$ (2 mm) and n_D^{21} 1.4685. We were unable to isolate any diol (V) from the acid aqueous solution.

Cyclization of geranylacetone under the action of kationite KU-2. A mixture of 20.0 g of geranylacetone and 15 g of kationite KU-2 containing 1.5 g of water was shaken in a hydrogenation flask at 90° . The course of the reaction was followed by the change in the refractive index and the content of keto group in the product. After three hours (n_D^{20} 1.5070, 12% of keto group) the reaction product was filtered from the resin and distilled at 1 mm. We obtained: Fraction I (2.4 g), b.p. $60-71^\circ$, n_D^{17} 1.4958, and 5.8% of keto group; Fraction II (9.0 g), b.p. $71-85^\circ$, n_D^{17} 1.5058; and 14.5% of keto group. Fraction II was treated chromatographically on alumina, and elution with petroleum ether gave 7.2 g of hydrocarbon (did not contain ketone); b.p. $65-70^\circ$; n_D^{21} 1.5090-1.5150; λ_{max} 240 m μ (ϵ 6440). Found: C 88.48; H 11.50; 11.55%. $\text{C}_{13}\text{H}_{20}$. Calculated: C 88.56; H 11.44%.

On being hydrogenated over platinum in acetic acid solution, the hydrocarbon obtained absorbed two molecular proportions of hydrogen and was found to be a bicyclic hydrocarbon. To prove the presence of (VI) in the mixture, 20.0 g of the hydrocarbon was dehydrogenated by passage over palladized charcoal at 380° . After several cycles the refractive index ceased to change. We obtained 0.4 g of 1,6-dimethylnaphthalene having n_D^{20} 1.5785-1.5805 and giving 0.35 g of picrate, m.p. $111-112^\circ$ (from ethanol). For the picrate of 1,6-dimethylnaphthalene the literature [17] gives m.p. $110-111^\circ$.

SUMMARY

1. A study was made of the cyclization of geranylacetone under the action of various acidic agents; optimum conditions for the reaction were found, and these permitted the preparation of the benzopyran derivative in 70-75% yield.
2. The proposed method is a stereospecific method for the cyclization of geranylacetone; from trans-geranylacetone it gives a benzopyran with trans-fusion of the rings, and from cis-geranylacetone it gives mainly a benzopyran with cis-fusion of the rings.
3. The cyclization of geranylacetone proceeds as simultaneous and antiparallel addition at the central C = C bond; the possible mechanism of this reaction is examined.

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RAMAN-SPECTRUM INVESTIGATION
OF SOME ACETYLENIC ALCOHOLS
AND THEIR ACETIC ESTERS

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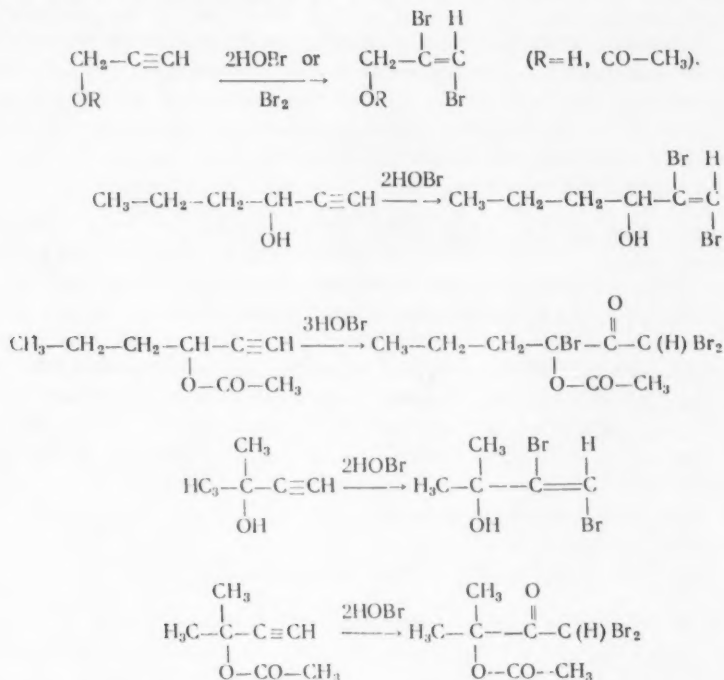
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The triple bonds of acetylenic alcohols, on the one hand, and of their acetic esters, on the other, differ in reactivity. Thus, on reaction of primary, secondary, and tertiary acetylenic alcohols with hypobromous acid they all form unsaturated dibromides; but the acetic esters of secondary and tertiary acetylenic alcohols react at the triple bond with formation of the corresponding saturated compounds, acetic esters of dibromo hydroxy ketones; only the acetic esters of primary acetylenic alcohols behave like the alcohols themselves and form unsaturated trans-dibromides [1]:



It was of interest to determine the physical basis of this difference in the reactivities of the triple bonds of acetylenic alcohols and their acetic esters, and this we attempted to do by investigating the Raman spectra of the following primary, secondary, and tertiary alcohols and their acetic esters:

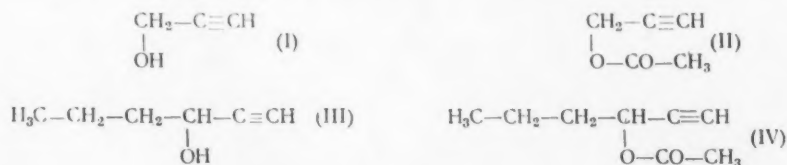


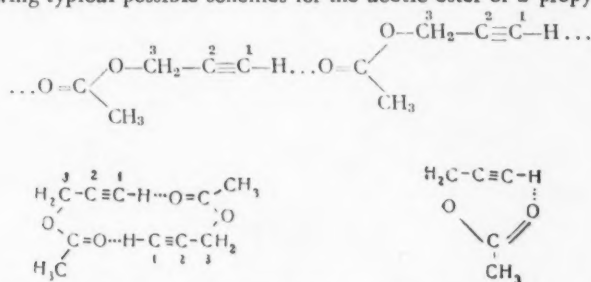
TABLE 1. Vibration Frequencies of Some Groups in Acetylenic Alcohols and Their Acetic Esters (cm^{-1})

Alcohol	O-H band	Maxima in O-H band	Frequency of free OH		$\text{C}\equiv\text{C}$	$\equiv\text{C}-\text{H}$	
			liquid	soln. in CCl_4		liquid	soln. in CCl_4
(I)	3200-3600	3410, 3570	3639	—	2117, 2127	3278, 3294, 3309	3312
(III)	3200-3600	3402, 3562	3619	3620	2102, 2111, 2120	3285, 3301, 3315	3311
(V)	3200-3600	3394, 3563	3620	3621	2112, 2123	3291, 3309	3311
(VII)	3200-3600	3380, 3549	3614	3614	2093, 2116	3286, 3298, 3312	3309
(IX)	3200-3600	3378, 3548	3613	3612	2093, 2105, 2120	3289, 3305, 3320	3306

Acetates	$\text{C}\equiv\text{C}$	$\text{C}=\text{O}$	$\equiv\text{C}-\text{H}$	
			liquid	soln. in CCl_4
(II)	2119, 2130	1731, 1742, 1754	3279, 3294, 3310	3311
(IV)	2118, 2128	1736, 1750, 1763	3236, 3256, 3271, 3287, 3305, 3319	3310
(VI)	2115, 2124	1733, 1744, 1755	3237, 3251, 3266, 3281, 3294, 3309, 3328	3309
(VIII)	2111, 2121	1737, 1746, 1757	3236, 3261, 3271, 3285, 3295, 3311, 3323, 3342	3308
(X)	2109, 2122	1738, 1747, 1757	3238, 3254, 3270, 3286, 3302, 3316, 3327	3306

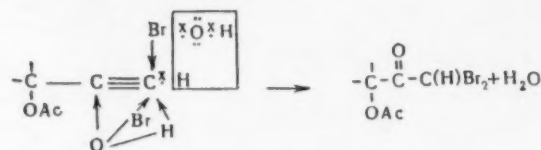
In the spectra of the liquid alcohols 2-3 frequencies are observed in the region of $\text{C}\equiv\text{C}$ frequencies, in the spectra of solutions of the alcohols in carbon tetrachloride there remains the high-frequency line, or it increases in intensity. In the spectrum of liquid 2-propyn-1-ol it would appear that two $\text{C}-\text{H}$ frequencies of the methylene group should be observed, but seven are actually observed in the region $2870-2977\text{ cm}^{-1}$, and these, moreover, are extremely intense; of these five frequencies in the region $2907-2977\text{ cm}^{-1}$ form an intense band (see spectra). a large number of lines is probably associated partially with the participation of 2-propyn-1-ol molecules in various kinds of complexes in which the CH_2 group occupies different positions, but basically this phenomenon is clearly determined by the above-noted intermolecular frequency modulation at hydrogen bonds, which has an effect even on the vibration of CH_2 bonds and possibly also on $\text{C}\equiv\text{C}$ bonds. The increase in the number of lines in the regions of the frequencies of the methylene and methylidyne groups is observed also in the spectra of the other alcohols.

In the acetic esters of the alcohols investigated hydrogen bonds are established by means of methylidyne and carbonyl groups; here there is possible formation of chain and cyclic complexes, and also of an intramolecular hydrogen bond, as in the following typical possible schemes for the acetic ester of 2-propyn-1-ol:



The acetic esters of the other alcohols will clearly form analogous complexes. The clearest manifestation of the hydrogen bond in the spectra of the acetic esters is formed by the structural $\text{C}-\text{H}$ bonds (see Table 1); whereas for 2-propynyl acetate it does not differ substantially from $\text{C}-\text{H}$ band of the alcohols investigated (its breadth is also equal to about 30 cm^{-1} , in which there are calculated to be three frequencies), for the acetic esters of the secondary and tertiary alcohols it differs substantially in breadth (it attains about 100 cm^{-1}) and in there being a substantially greater number of frequencies calculated to be present (6-8), and in this the influence of the acetyl group is clearly manifest. The $\text{C}\equiv\text{C}$ and $\text{C}=\text{O}$ bonds are characterized in the spectra of acetic esters by 2-3 frequencies. The presence of many frequencies in the spectra of these bonds is probably partially associated with their participation in various kinds of associated complexes, but in the main it is the result of the above-noted frequency modulation (particular of $\equiv\text{C}-\text{H}$ bonds) by intermolecular vibrations at hydrogen bonds. In the spectra of solutions of the acetic ester in carbon tetrachloride the high-frequency line of these groups is preserved, which is associated with breakdown of the complexes and the presence in the solutions of mainly monomeric molecules.

The main and essential spectral difference between the acetic esters of secondary and tertiary alcohols, on the one hand, and the alcohols and the acetic ester of the primary alcohol, on the other, lies in the greater breadth of the structural $\equiv\text{C}-\text{H}$ band, mainly due to the position of its low-frequency edge, which reflects the more acidic properties of this bond in these vibrational states [3]. This physical peculiarity of the $\equiv\text{C}-\text{H}$ bond of the acetic esters of secondary and tertiary alcohols investigated is probably related to their above-noted special chemical behavior toward hypobromous acid. The protonized (acidic) hydrogen atom of the $\equiv\text{C}-\text{H}$ bond of the acetic esters of secondary and tertiary alcohols readily reacts with the extremely weak hypobromous acid: nucleophilic addition of the hydroxyl of HOBr to the protonized hydrogen atom of the $\equiv\text{C}-\text{H}$ bond occurs with subsequent electrophilic addition of Br to C-1. This addition communicates an impulse to the electron system of the $\text{C} \equiv \text{C}$ bond in the direction of the C-1 atom, which intensifies the unmasking of the positive nucleus of the C-2 atom and facilitates nucleophilic addition of the oxygen atom of another HOBr molecule to the C-2 atom with a further impulse of the electron system of $\text{C} \equiv \text{C}$ in the direction of the C-1 atom, which stimulates subsequent electrophilic addition, probably of the positive Br and H ions, to C-1.



EXPERIMENTAL

The physical properties of the compounds investigated are given in Table 2.

The Raman spectra were determined with an ISP-51 Soviet spectrograph with a central camera and with a Hilger E 612 spectrograph; the exciting radiation was the mercury blue line at 4358 Å.

2-Propyn-1-ol (I). $\Delta\nu \text{ cm}^{-1}$: 212(3*)—219(5*)—231(4*) band 315(8m), 557(4), 621—710 (3, band; on it, frequencies 632—647*—663*—679*—691*), 919(6), 1023(3*)—1034(6*)—1047(4*) полоса, 1227(3**), 1240(3**), 1349(4*), 1363(4*), 1371(1*), 1417(1), 1447(2*), 1454(5*), 1465(4*), 2117(10**), 2127(10**), 2870(4*), 2881(8*), 2907(3**), 2924(10**), 2941(10**), 2959(10**), 2977(3**) полоса, 3278(3*), 3294(5*), 3309(3*), ~ 3200—3600 (3band; on it are the maxima ~ 3410, 3570), 3639(0).

2-Propyn-1-ol Acetic Ester (II). $\nu \Delta \text{ cm}^{-1}$: 236(5 ш, дв), 273(3*), 285(4*), 293(3*), 315(6**), 325(6**), 362(0), 390(2*), 403(3*), 508(0), 519(2*), 533(3*), 557(0), 635(5), 646(0*), 658(1*), 673(2* дв), 706(0), 742(0), 832(7), 894(3*), 907(3*), 939(4**), 949(4**), 973(0), 988(0), 1002(0), 1019(0*), 1035(7* ш, дв), 1048(0*), 1086(0), 1103(0), 1221(3*), 1233(3*), 1249(0), 1273(2), 1360(5* дв), 1381(3* дв), 1409(0), 1433(6*), 1445(3* p), 1456(3*), 1731(5**), 1742(5**), 1754(1**), 2119(10*), 2130(10*), 2875(3**), 2888(3*), 2930(10*), 2940(10*), 2952(2*), 2990(3*), 3017(0), 3039(1), 3279(3*), 3294(3*), 3310(3*).

1-Hexyn-3-ol (III). $\Delta\nu \text{ cm}^{-1}$: 202(1*), 215(3*), 226(3*), 241(6*), 252(4*), 265(1**), 278(3*), 291(1**), 345(1), 366(4 p), 408(2*), 421(2*), 433(2*), 565(2**), 575(3**), 582(2**), 625(3*), 645(3*), 665(3*), 743(2), 803(3 дв), 825(0), 846(2), 873(4), 889(0), 900(5*), 910(2*), 925(2*), 985(1**), 1003(3**), 1023(1**), 1040(3**), 1066(6), 1090(0), 1105(5*), 1117(3*), 1216(1), 1252(1), 1297(5*), 1312(1*), 1329(3*), 1435(3**), 1446(5**), 1455(3**), 1464(1**), 2102(8*), 2111(10* p), 2120(5*), 2712(0), 2736(1), 2859(2*), 2868 (7* p), 2881(3*), 2892(1*), 2906(10*), 2918(10*), 2932(9*), 2944(9*), 2955(3*), 2964(3*), 3285(3**), 3301(3**), 3315(3**), ~ 3200—3600(2, band; on it are the maxima ~ 3402, 3562), 3619(1*).

1-Hexyn-3-ol Acetic Ester (IV). $\Delta\nu \text{ cm}^{-1}$: 171(1*), 180(2*), 190(3*), 204(2*), 240(2**), 254(1**), 286(5), 312(2*), 327(2*), 394(2**), 412(1**), 433(2**), 443(1*), 506(0), 527(2*), 541(4*), 554(5*), 625(3**), 635(4**), 652(5**), 666(3**), 678(1**) band 825(5 дв), 848(0), 918(7*), 931(6*), 941(1*), 959(0**), 973(2**), 988(1**), 1012(2*), 1025(3*), 1034(2*), 1062(4**), 1073(4*), 1109(5 дв), 1142(3 дв), 1236(1), 1303(5* дв), 1320(4* дв), 1342 (4* дв), 1436(7**), 1449(8**), 1462(3**), 1736(4*), 1750(4*), 1763(2*), 2118(10**), 2128(10**), 2743(1), 2867(2*), 2878(7*), 2910(1*), 2920(5*), 2934(10*), 2948(5*), 2976(3*), 3236(1**), 3256(1**), 3271(3**), 3287(3**), 3305(3**), 3319(1**).

4-Methyl-1-pentyn-3-ol (V). $\Delta\nu \text{ cm}^{-1}$: 152(8*)—161(8*)—171(5*) band 218(5**) — 230(5**) — 242(2**) band 274(0), 339(5), 373(2*), 382(2*), 403(1), 436(1), 449(1*), 469(1*), 492(1), 515(3p), 556(1), 576(2*), 589(3*), 616(3**) — 628(2**) — 643(1**) — 656(2**) band 708(1), 767(0), 801(7), 826(5), 856(0), 895(4 дв), 961(5*), 972(1*), 987(4*), 1006(0), 1025(1), 1033(5*), 1048(4*), 1073(0), 1090(3*), 1102(3*), 1109(3* p), 1122(5*), 1137(5*), 1165(1**), 1182(3**), 1264(1*), 1280(3*), 1296(2*), 1318(1*), 1374(2 дв, ш), 1390(1), 1451(7*), 1464(6*), 2112(10**), 2123(10**), 2720(1), 2761(1).

*The abbreviations given with the intensities are: m broad line; p, sharp line; дв doublet; asterisks denote lines on a background that is common to neighboring lines denoted by the same number of asterisks.

TABLE 2. Physical Properties of Some Acetylenic Alcohols and Their Acetic Esters

No.	Compound	B.p. in °C (p in mm)	n_D^{20}
I	$\text{CH}_2=\text{C}\equiv\text{CH}$ OH	112—114 (760)	1,4320
II	$\text{CH}_2=\text{C}\equiv\text{CH}$ O—CO—CH ₃	122—124 (760)	1,4180
III	$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}-\text{C}\equiv\text{CH}$ OH	143—144 (760)	1,4358
IV	$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}-\text{C}\equiv\text{CH}$ O—CO—CH ₃	162 (760)	1,4250
V	$\text{H}_3\text{C}-\text{CH}-\text{CH}-\text{C}\equiv\text{CH}$ CH ₃ OH	132—133 (760)	1,4352
VI	$\text{H}_3\text{C}-\text{CH}-\text{CH}-\text{C}\equiv\text{CH}$ CH ₃ O—CO—CH ₃	155—156 (760)	1,4242
VII	$\text{H}_3\text{C}-\text{C}-\text{C}-\text{CH}$ OH CH ₃	103 (760)	1,4213
VIII	$\text{H}_3\text{C}-\text{C}-\text{C}\equiv\text{CH}$ O—CO—CH ₃	131—132 (760)	1,4200
IX	$\text{H}_3\text{C}-\text{CH}_2-\text{C}-\text{C}-\text{CH}$ OH CH ₃	121 (760)	1,4320
X	$\text{H}_3\text{C}-\text{CH}_2-\text{C}-\text{C}\equiv\text{CH}$ O—CO—CH ₃	48—50 (13)	1,4270

2873(10*), 2890(1*), 2909(9*), 2927(1*), 2942(3*), 2966(7*), 2982(5*), 3291(3**), 3309(4**), ~ 3200—3600 (2, band, on it are the maxima ~ 3394, 3563), 3620 (1)
 4-Methyl-1-pentyn-3-ol Acetic Ester (VI) $\Delta\nu$ cm⁻¹ 142—167(8 m), 248(4*), 259(4*), 272(4*), 289(2*), 321(3**), 335(3**), 363(3), 388(3*), 402(3*), 428(0), 452(2*), 460(2*), 513(3**), 528(1**), 558(5), 597(3*), 608(3*), 619(3*), 636(3**), 649(3**), 665(3**), 705(1), 813(3*), 825(3*), 896(7p**), 906(5p**), 916(7p**), 937(0), 961(3), 982(3), 998(1), 1026(4), 1056(0), 1082(0), 1104(3), 1125(3), 1150(3 дв), 1185(3 m), 1217(0), 1230(1), 1243(3), 1280(4*), 1300(4*), 1336(4**), 1351(4**), 1450(7*), 1466(7*), 1733(2**), 1744(4**), 1755(2**), 2115(10*), 2124(10*), 2702(0), 2726(1), 2744(0), 2875(6*), 2909(6*), 2941(10*), 2964(6*), 2980(6*), 2992(1*) 3236(1**), 3251(1**), 3266(1p**), 3281(1p**), 3294(3p**), 3309(3p**), 3328(2p**).

2-Methyl-3-butyn-2-ol (VII). $\Delta\nu$ cm⁻¹ 179(10*), 187(10*), 197(5*), 210(3*), 363(4), 378(0), 392(0*), 406(4*), 416(5**), 427(5**), 560(6), 628(1*), 646(3*), 659(3*), 677(1), 709(10), 895(6), 932(5), 964(7), 1134 (3*), 1153(2*), 1168(5*), 1179(5*), 1214(2), 1445(8*), 1460(8*), 2093(5**), 2116(10**m), 2716(3), 2868(4*), 2880(4*), 2902(2*), 2920(7*), 2942(10**), 2980(10**), 2992(10**), 3286(3*), 3298(4*), 3312(4*), ~ 3200—3600 (3, band, on it are the maxima ~ 3380, 3549), 3614(0).

2-Methyl-3-butyn-2-ol Acetic Ester (VIII) $\Delta\nu$ cm^{-1} : 166(2*), 188(8*ш, дн), 215(6*ш), 336(5), 368(4), 392(4), 423(4), 536(4*), 550(4*), 572(0), 618(3), 648(10), 729(3*), 740(4*), 750(3*), 833(1**), 846(6р**), 929(3*), 940(4*), 968(6), 1016(4ш), 1139(5), 1198(4), 1231(1**), 1246(2**) — 1262(2**) band 1299(1) — 1347(0) — 1369(1) — 1389(1) — 1409(1) — 1431(1) band 1453(9ш), 1737(2*), 1746(5*), 1757(2*), 2111(10**), 2121(10**), 2152(1*), 2165(1*), 2719(3), 2762(0), 2864(2*), 2878(4*), 2894(3*), 2926(7*), 2939(10*), 2953(7*), 2987(6*), 2999(6*), 3015(2*), 3026(5*), 3236(1**), 3261(1**), 3271(2**), 3285(3**), 3295(3**), 3311(2**), 3323(1**), 3342(1**).

3-Methyl-1-pentyn-3-ol (IX) $\Delta\nu$ cm^{-1} 160(7*), 169(7*), 186(10р), 195(10р*), 205(5р), 213(3*), 264(3**), 275(3**), 285(3**), 375(4*), 358(4*), 405(4**), 418(3**), 431(4**), 444(3**), 456(2**), 468(2**), 556(4дн), 591(4дн), 644(1*), 658(4*), 690(9ш), 712(4), 753(0), 788(3), 899(4дн), 922(5дн), 1000(7), 1055(4), 1104(3*) — 1118(4*) — 1122(3*) — 1152(4*) — 1169(4*) band 1270(1**), 1279(3**), 1289(3**), 1442(5*), 1452(9*), 1465(3*), 2093(1**), 2105(10**), 2120(10**), 2736(3ш), 2847(1*), 2869(1*), 2886(7*дн), 2913(2*), 2931(3*), 2944(10*), 2951(2*), 2970(2р), 2983(10*), 2992(5*), 3289(2**), 3305(5**), 3320(2**), ~ 3200—3600(3, band, on it are the maxima ~ 3378 & 3548), 3613(0).

3-Methyl-1-pentyn-3-ol Acetic Ester (X) $\Delta\nu$ cm^{-1} 171(2*), 179(2*), 191(1**), 200(3**), 212(1**), 274(2*), 296(1*), 338(5), 366(4), 395(2), 419(3*), 428(3*), 463(2дн), 516(2), 531(3*), 545(2*), 560(3*), 612(3**), 623(1**), 638(8**), 658(4**дн), 733(4ш), 783(2), 846(1*), 857(7*), 912(3дн), 945(4ш), 999(6*), 1013(4*), 1038(0), 1058(4), 1109(3**), 1129(5* дн), 1161(2**), 1176(1**), 1191(3**), 1210(2*), 1220(2*), 1239(2**), 1252(2**), 1288(2*), 1300(3*), 1440(9**), 1454(4**), 1466(2**), 1738(2*), 1747(4*), 1757(2*), 2109(10**), 2122(10**), 2718(1), 2739(2), 2870(1*), 2883(5*), 2913(2*), 2932(10*), 2944(10*), 2979(6*), 2991(6*), 3022(4*), 3238(1**), 3254(2**), 3270(3**), 3286(3**), 3302(3**), 3315(1**), 3327(1**).

SUMMARY

The formation of the acetic esters of tri- and di-bromo ketols by the action of HOBr on the acetic esters of secondary and tertiary acetylenic alcohols is due to the particularly strongly protonized (acidic) hydrogen atom of the methylidyne group $\equiv \text{C}-\text{H}$, which results from profound frequency modulation of the vibrations of the latter by the low-frequency intermolecular vibrations at the hydrogen bonds.

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PRODUCTS OF THE HYDROGENATION

OF 1-METHYL-5-(4-METHYLAMINO-1-BUTENYL)-2(1H)-PYRIDONE

Ya. L. Gol'dfarb and V. V. Kiseleva

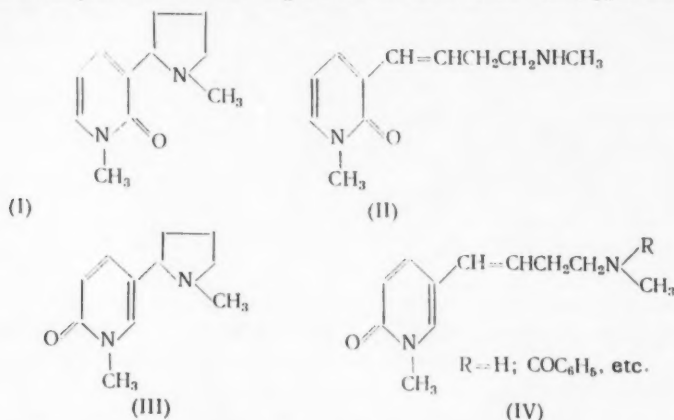
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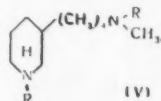
No. 12, pp. 2208-2214, December, 1960

Original article submitted July 21, 1959

In a brief communication [1] we described Py-N-methylmetanicotone and some of its derivatives, which were prepared from Py-N-methylnicotone, which was described by Karrer as 1-methyl-3-(1-methyl-2-pyrrolidinyl)-2(1H)-pyridone (I) [2]. For this reason we attributed the structure of the substituted 2(1H)-pyridone (II) to the corresponding Py-N-methylnicotone. However, work by Japanese authors [3] and our own recent results [4] convinced us the substance that Karrer had was actually Py-N-methyl- α' -nicotone (III), i.e., 1-methyl-5-(1-methyl-2-pyrrolidinyl)-2(1H)-pyridone, so that our products must be assigned the structure of the 2(1H)-pyridones (IV):



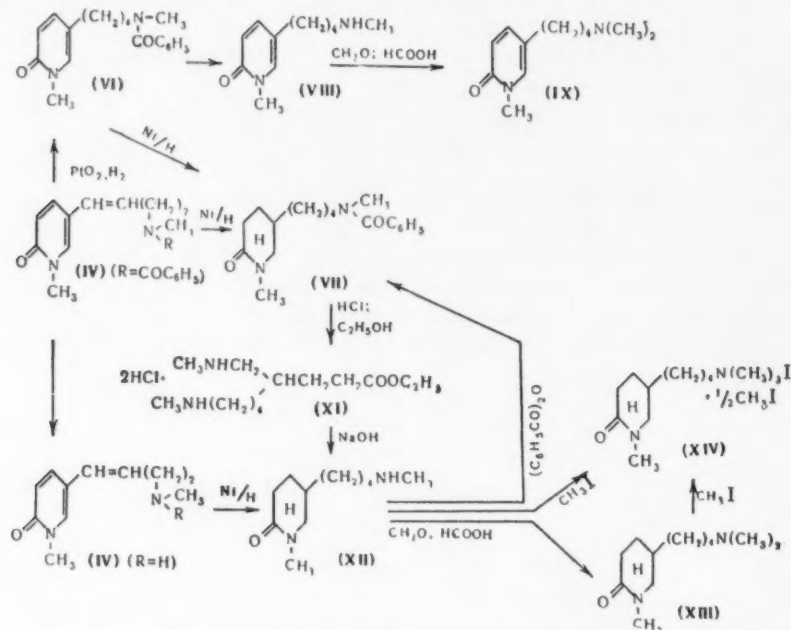
We undertook the investigation of 1-methyl-5-(4-methylamino-1-butenyl)-2(1H)-pyridone (IV; R = H) and its derivatives with the object of finding physiologically active substances that are less toxic than nicotine and metanicotone. In the present paper we report on some products of the hydrogenation of 5-(4-amino-1-butenyl)-1-methyl-2(1H)-pyridone and its derivatives. The study of such substances is all the more interesting in that substances of high physiological activity have been found among the hydrogenated metanicotones. Thus, Phillips [5,6] in the reductive cleavage of nicotine alkoiodides (or of nicotine itself with subsequent alkylation) obtained a series of dialkyl derivatives of 3-(4-methylaminobutyl)piperidine (V) and their bisquaternary ammonium salts which had a powerful ganglion-blocking action and produced a great and prolonged reduction of blood pressure.



It was shown that of the alkyl derivatives the highest activity combined with the lowest toxicity was possessed by the methyl derivatives, particularly 3-(4-dimethylaminobutyl)-1-methylpiperidine. The corresponding bissecondary diamines also possess hypotensive activity. The activity of the bismethiodides of the compound (V; R = CH₃) was later reported also by other authors [7].

By the hydrogenation in alcoholic solution of 1-methyl-5-(4-N-methylbenzamido-1-butenyl)-2(1H)-pyridone (IV; R = COC₆H₅) with hydrogen in presence of Adams platinum oxide, we obtained a good yield of 1-methyl-5-(4-N-methylbenzamido-1-butenyl)-2(1H)-pyridone (VI) and a little 1-methyl-5-(4-N-methylbenzamido-1-butenyl)-2-piperidone (VII).

By the action of excess of Raney nickel in alcohol on 1-methyl-5-(4-N-methylbenzamidobutyl)-2(1H)-pyridone (VI), and also on 1-methyl-5-(4-N-methylbenzamido-1-butenyl)-2(1H)-pyridone or its hydrochloride [1], the hydrogenation was extended to the pyridine ring and 1-methyl-5-(4-N-methylbenzamidobutyl)-2-piperidone (VII) was formed in good yield. It should be noted that under the given conditions the reduction of the CO group of the ring does not occur, which characteristic for 1-methyl-2(1H)-pyridones [8], but not for 1-methyl-4(1H)-pyridones, which under the action of Raney nickel under pressure give the corresponding 4-piperidinols [9]. Under other conditions 1-methyl-2(1H)-pyridones are reduced to 1-methyl-2-piperidinols [10].



By the hydrolysis of the benzoyl derivative (VI) with hydrochloric acid we obtained 1-methyl-5-(4-methylaminobutyl)-2(1H)-pyridone dihydrochloride, from which by treatment with alkali we isolated the free base (VIII), a fairly mobile colorless liquid with marked basic properties; it formed a monopicrate. By the methylation of the base (VIII) with formaldehyde in formic acid we obtained 5-(4-dimethylaminobutyl)-1-methyl-2(1H)-pyridone (IX). On treatment of the base (VIII) with excess of methyl iodide we isolated a quaternary salt which corresponded in analysis to the hydriodide of 5-(4-dimethylaminobutyl)-1-methyl-2(1H)-pyridone methiodide (X).

On hydrolysis of the benzoyl group of 1-methyl-5-(4-N-methylbenzamidobutyl)-2-piperidone (VII), as would be expected from its lactam nature, the piperidone ring was opened [11], and on subsequent treatment with alcohol we isolated the dihydrochloride of the ethyl ester of the diamino acid (XI), m.p. 152°. The base obtained in the usual way from this salt was found to be 1-methyl-5-(4-methylaminobutyl)-2-piperidinone (XII), the dehydrochloride of which melted at 166-168°. Such a tendency for the ready closure of a pyridone ring by a diamino acid is in accord with data in the literature for δ -amino acids [12].

On treating the base (XII) with benzoic anhydride, we obtained the above-described 1-methyl-5-(4-N-methylbenzamidobutyl)-2-piperidone (VII), and under the action of excess of methyl iodide we obtained the corresponding quaternary salt (XIV). We obtained 1-methyl-5-(4-methylaminobutyl)-2-piperidone (XII) also by the hydrogenation of 1-methyl-5-(4-methylamino-1-butenyl)-2(1H)-pyridone (IV; R = H), which was described in [1], in presence of Raney nickel; unlike (VIII), under comparable conditions (XII) gives a di- and not a mono-picrate. Methylation of the base (XII) with formaldehyde in formic acid gives 5-(4-dimethylaminobutyl)-1-methyl-2-piperidone (XIII), which gives the quaternary salt (XIV) under the action of excess of methyl iodide.

EXPERIMENTAL

Hydrogenation of 1-methyl-5-(4-N-methylbenzamido-1-butenyl)-2(1H)-pyridone (IV; R = COC_6H_5). 1-Methyl-5-(4-N-methylbenzamido-1-butenyl)-2(1H)-pyridone (7.5 g; m.p. 98°) was hydrogenated as a solution in 40 ml

of alcohol at 18° and atmospheric pressure with hydrogen in presence of Adams platinum oxide in a hydrogenation flask with shaking. About 13% excess of hydrogen was supplied. The solution was decanted, and the precipitate was washed several times with alcohol; the combined solutions were vacuum-evaporated. The residual pale-yellow oil was washed several times with dry ether, after which it crystallized. We obtained 7.0 g (92.5%) of a substance of m.p. 109-111°. After crystallization from ether containing a few drops of alcohol it had m.p. 112-113° (elongated hexahedral plates). The substance was readily soluble in water, alcohol, chloroform, and benzene and sparingly soluble in hot ether, heptane, and petroleum ether. The pH of an aqueous solution was about 6 (universal indicator). Found: C 71.88; 72.11; H 7.48; 7.29%. $C_{18}H_{22}O_2N_2$. Calculated: C 72.48; H 7.38%. The analysis corresponds to 1-methyl-5-(4-N-methylbenzamidoethyl)-2(1H)-pyridone (VI).

From the ethereal solution, after removal of solvent, we isolated 0.45 g of a light-yellow oil, which later crystallized. After washing it with petroleum ether we obtained 0.4 g of a substance of m.p. 50-52°, which was found to be identical to 1-methyl-5-(4-N-methylbenzamidoethyl)-2-piperidone (VII) obtained by the reduction of 1-methyl-5-(4-N-methylbenzamidoethyl)-2(1H)-pyridone with Raney nickel; yield 5%.

Hydrolysis of 1-methyl-5-(4-N-methylbenzamidoethyl)-2(1H)-pyridone (VI). A solution of 4.8 g of (VI) in 38.5 ml of 1 : 1 hydrochloric acid was boiled over a gauze for ten hours. The cooled solution was extracted with ether. From the ether we isolated 1.8 g (92%) of benzoic acid. The hydrochloric acid solution was vacuum-evaporated to dryness; the residual viscous oil rapidly crystallized in the form of needles; yield 4.0 g (93%) of unpurified hydrochloride. After crystallization from absolute alcohol (with addition of charcoal) we obtained 1.35 g of a crystalline substance, m.p. 171-172° (decomp.), 1.3 g of product of m.p. 169-171°, and 1 g of a more contaminated product. The yield of the crystallized substance was 2.65 g (62%). After recrystallization it had m.p. 171° (decomp). Found: C 49.27; 49.55; H 7.37; 7.25; Cl 26.25; 26.95%. $C_{11}H_{20}ON_2Cl_2$. Calculated: C 49.44; H 7.49; Cl 26.59%. The analysis corresponds to 1-methyl-5-(4-methylaminobutyl)-2(1H)-pyridone dihydrochloride

This dihydrochloride (2.5 g) was treated with a saturated solution of potassium carbonate, and the oil layer formed was extracted with isobutyl alcohol. The turbid oil remaining after the removal of solvent was treated with hot ether. After the separation of impurities and the removal of ether there remained 1.55 g (86%) of a light-yellow oil, which was vacuum-distilled. We obtained 1.35 g of a fairly mobile colorless oil, b.p. 173° (2 mm); yield of pure product 75%. Found: C 68.00; 67.92; H 9.40; 9.27; N 14.73; 14.87%. $C_{11}H_{18}ON_2$. Calculated: C 68.04; H 9.28; N 14.43%. Determination of the equivalent weight by titration of a weighed sample of the base with 0.1 N H_2SO_4 to Bromothymol Blue gave 199 and 207; the calculated molecular weight is 194.

From 0.3 g of the base in an alcoholic solution of HCl we obtained 0.35 g of a substance of m.p. 171-172°, identical with the original 1-methyl-5-(4-methylaminobutyl)-2(1H)-pyridone dihydrochloride. The picrate prepared from an alcoholic solution of the base had m.p. 164-165° (needles from alcohol). Found: N 16.49; 16.58%. $C_{17}H_{21}O_8N_5$. Calculated for the monopicrate: N 16.55%.

When the base (VIII) was heated with excess of methyl iodide the corresponding quaternary salt was isolated in the form of the dipicrate of composition $C_{25}H_{28}N_8O_{15}$; m.p. 130-131°. Found: N 16.47; 16.43%. $C_{25}H_{28}N_8O_{15}$. Calculated: N 16.47%. The molecular weight, found spectrophotometrically, was 676; the value calculated for the dipicrate is 680.

Treatment of the dipicrate with hydriodic acid gave the quaternary salt (X), m.p. 200-202°, which corresponded in analysis to the hydriodide of 5-(4-dimethylaminobutyl)-1-methyl-2(1H)-pyridone methiodide. Found: I 52.90; 52.56%. $C_{13}H_{23}N_2OI \cdot HI$. Calculated: I 53.20%.

Reduction of 1-methyl-5-(4-N-methylbenzamidoethyl)-2(1H)-pyridone (VI) with Raney nickel. About 25 g of Raney nickel paste was introduced under alcohol into a three-necked flask fitted with stirrer, reflux condenser, and dropping funnel, and it was stirred in the alcohol and heated in a water bath while gradual addition (one hour) was made of an alcoholic solution of 5 g of 1-methyl-5-(4-N-methylbenzamidoethyl)-2(1H)-pyridone (VI). The mixture was heated in the water bath for a further four hours. The mixture was cooled, and the catalyst was rapidly filtered off and washed with alcohol. The alcoholic solutions were vacuum-evaporated, and the residual turbid oil was treated several times with hot dry ether; inorganic salts were separated, and the clear light-yellow oil obtained after removal of solvent (4.3 g) crystallized on long standing; m.p. 53-56°. After purification by dissolution in ether and precipitation with petroleum ether under strong cooling, the melting point was 64-65°. The substance was readily soluble in water, alcohol, chloroform, and pyridine, less readily soluble in benzene and ether, and insoluble in petroleum ether and heptane. Its aqueous solution was almost neutral to litmus, the pH to universal

indicator being 6-6.5. Found: C 71.43; 71.38; H 8.81; 8.69; N 9.27; 9.02%. $C_{18}H_{26}N_2O_2$. Calculated: C 71.52; H 8.61; N 9.27%. The analysis corresponds to 1-methyl-5-(4-N-methylbenzamido-1-butenyl)-2(1H)-pyridone (VII). The substance does not contain active hydrogen.

The same substance was obtained in 94-96% yield by the reduction of 1-methyl-5-(4-N-methylbenzamido-1-butenyl)-2(1H)-pyridone (IV; $R = COC_6H_5$) in alcohol with Raney nickel, and also its monohydrochloride [1] in methanol.

Hydrolysis of 1-methyl-5-(4-N-methylbenzamido-1-butenyl)-2-piperidone (VII). A solution of 10 g of 1-methyl-5-(4-N-methylbenzamido-1-butenyl)-2-piperidone (VII) in 85 ml of 1 : 1 hydrochloric acid was refluxed for five hours. From the cooled solution 3.75 g (94%) of benzoic acid was extracted with ether. The hydrochloric acid solution was vacuum-evaporated, and moisture was removed from the residual oil; the oil was dissolved in absolute alcohol, and with cooling dry ether was added to the solution. We obtained 3.85 g of a crystalline substance of m.p. 151-153°, 3.75 g of a substance of lower melting point (136-140°), and 0.5 g of substance of m.p. 126-133°. The yield of unpurified product was 8.1 g (90%). After purification by recrystallization from a mixture of alcohol and ether we isolated a substance with a constant melting point of 152.5-154.5°, which was found by analysis to be ethyl 8-methylamino-4-(methylaminomethyl)octanoate dihydrochloride. The yield of pure substance was 5.6 g (62%). Found: C 48.81; 48.87; H 9.29; 9.57; N 8.85; 8.98; Cl 22.31; 22.67%. $C_{13}H_{20}N_2O_2 \cdot Cl_2$. Calculated: C 49.21; H 9.46; N 8.86; Cl 22.40%.

An aqueous solution of 3 g of the dihydrochloride of m.p. 151-153° was made alkaline with 40% KOH under cooling and was saturated with potassium carbonate. The light-colored oil which floated up was extracted with isobutyl alcohol, the dried solution was vacuum-evaporated, and the residual turbid oil was extracted with hot dry ether. The light-colored oil (1.75 g) purified in this way was dried to constant weight and then corresponded in analysis to 1-methyl-5-(4-methylaminobutyl)-2-piperidone (XII). Found: C 66.37; 66.11; H 11.11; 11.12; N 14.17; 14.25%. $C_{11}H_{22}ON_2$. Calculated: C 66.67; H 11.11; N 14.14%. The substance did not contain active hydrogen. On addition of alcoholic HCl to an alcoholic solution of the base and precipitation with ether we obtained the hydrochloride, which after purification melted at 166-168° and corresponded in analysis to 1-methyl-5-(4-methylaminobutyl)-2-piperidone dihydrochloride. Found: C 48.62; 48.84; H 8.89; 9.06; N 10.14; 10.03; titration Cl 26.31; 26.66%. $C_{11}H_{22}ON_2 \cdot 2HCl$. Calculated: C 48.71; H 8.86; N 10.33; Cl 26.20.

By the action of methyl iodide on 2 g of the base (XII) in methanol we obtained the methiodide which after crystallization from alcohol melted at 192-193° and corresponded in analysis to the formula $C_{12}H_{24}ON_2 \cdot 1\frac{1}{2} CH_3I$. Found: C 37.81; 37.87; H 6.89; 6.78; I 43.23; 43.98%; I determined by microtitration: 44.28; 43.92%. $C_{13.5}H_{28.5}N_2I_{1.5}O$. Calculated: C 38.12; H 6.71; I 44.82%.

On benzoylating 0.9 g of the base (XII) with benzoic anhydride in benzene solution we succeeded in isolating 1-methyl-5-(4-N-methylbenzamido-1-butenyl)-2-piperidone (VII), m.p. 52-53°, undepressed by admixture of the sample obtained previously (above).

Reduction of 1-methyl-5-(4-methylamino-1-butenyl)-2(1H)-pyridone (IV; $R = H$) with excess of Raney nickel in methanol. The experiment was carried out as described for the reduction of (VI) (above). From 11.8 g of the base (IV; $R = H$), b.p. 179-182 (2 mm), we obtained 11.15 g (90%) of a clear light-yellow oil, from 10 g of which by two vacuum distillations at 3 mm we obtained a colorless oil; Fraction I (1.85 g), b.p. 160-162°; Fraction II (5.55 g), b.p. 162-164°; Fraction III (1.05 g), b.p. 167-175°.

Analysis of Fraction II; found: C 66.78; 67.04; H 10.86; 11.08; N 14.34; 14.30%. $C_{11}H_{22}ON_2$. Calculated: C 66.67; H 11.11; N 14.14%. The analysis corresponds to the base (XII). In another experiment: b.p. 145-147° (1.5 mm).

The picrate, prepared in alcoholic solution, had m.p. 162-164°; after recrystallization from alcohol; m.p. 166-167°. It corresponded in analysis to 1-methyl-5-(4-methylaminobutyl)-2-piperidone dipicrate. Found: N 17.05; 17.05%. $C_{23}H_{28}O_{15}N_8$. Calculated: N 17.07%.

Methylation of 1-methyl-5-(4-methylaminobutyl)-2-piperidone (XII) with formaldehyde in formic acid. With application of cooling, 4 g (0.02 mole) of the base (XII) was mixed with 8.2 ml of 85% formic acid. After the addition of 6 ml of 35% formaldehyde the mixture was heated for four hours in a boiling water bath. A further 8.2 ml of 85% formic acid and 5.0 ml of 35% formaldehyde were then added, and heating was continued further for six hours. When cool, the mixture was acidified with 6 ml of concentrated hydrochloric acid, the solution was vacuum-evaporated to dryness, and moisture was removed by distillation with benzene. On being left in a vacuum

desiccator, the residual colorless oil (5.6 g) partially crystallized, and 0.5 g of the substance m.p. 112-116° (the melt became clear only at about 130°), was purified by precipitation with ether from a cooled alcoholic solution. The melting point of the resulting crystals was 125-127°. Found: C 50.91; 50.99; H 9.25; 9.10; Cl 23.77; 23.03%. $C_{12}H_{26}ON_2Cl_2$. Calculated: C 50.53; H 9.12; Cl 24.91%. From 0.5 g of the unpurified hydrochloride we prepared the picrate (in alcohol); it had m.p. 107-109° and corresponded in analysis to 5-(4-dimethylaminobutyl)-1-methyl-2-piperidone dipicrate. Found: 16.86; 16.50%. $C_{24}H_{30}O_{15}N_8$. Calculated: N 16.75%. For the monopicrate N 15.65%.

Caustic alkali was added with cooling to a solution of 4.5 g of the unpurified hydrochloride in water until the reaction to phenolphthalein was distinctly alkaline; the solution was saturated with potassium carbonate, and extracted with ether. The ethereal solution was dried, and ether was vacuum-distilled off. We obtained 2.95 g of a clear light-yellow oil, and 0.6 g of this was vacuum-distilled at 2 mm: Fraction I (0.1 g), b.p. 134°; Fraction II (0.1 g), b.p. 134.5-135°; Fraction III (0.3 g), b.p. 135.5-138°. Fraction II, a colorless oil, was analyzed. Found: C 67.87; 67.77; H 11.51; 11.26; N 13.46; 13.08%. $C_{12}H_{24}ON_2$. Calculated: C 67.79; H 11.32; N 13.21%. The analysis corresponds to 5-(4-dimethylaminobutyl)-1-methyl-2-piperidone (XIII).

The picrate prepared from Fraction III (m.p. 107-109°) showed no depression of melting point in admixture with the picrate prepared previously from the unpurified hydrochloride (m.p. 107-109°).

Methylation of 5-(4-dimethylaminobutyl)-1-methyl-2-piperidone (XIII) with methyl iodide. Methyl iodide (1.5 ml) was added to a solution of 1.5 g of the undistilled base obtained in the preceding experiment in absolute methanol, and the mixture was refluxed for two hours in a water bath, after which a further 1.3 ml of methyl iodide was added and heating was continued further for two hours. A further 2.2 ml of methyl iodide was then added, and boiling was continued further for 16 hr. In all, 5 ml of methyl iodide was added and boiling was continued for 20 hr. Methanol and excess of methyl iodide was vacuum-distilled off; the residual oil solidified on standing. After crystallization from alcohol we obtained 1.2 g of crystals of m.p. 187-190° and 0.15 g of m.p. 180-184°. Melting point after recrystallization 191-193°. Found: I by microtitration 44.07; 44.26%. $C_{13}H_{24}ON_2I \cdot \frac{1}{2}CH_3I$. Calculated: I 44.82%. The substance showed no depression of melting point in a mixture test with the methiodide (XIV) (m.p. 192-193°) obtained earlier by the action of methyl iodide on 1-methyl-5-(4-methylaminobutyl)-2-piperidone.

Methylation of 1-methyl-5-(4-methylaminobutyl)-2(1H)-pyridone (VIII) with formaldehyde in formic acid. The experiment was carried out as described above for the base (XII). From 1.8 g of the base (VIII) we obtained 2.5 g (95%) of a colorless substance, which after crystallization from absolute alcohol gave 1.6 g of crystals of m.p. 185-187° (in a sealed capillary), 0.35 g of m.p. 182-184°, and 0.25 g of m.p. 178-180°. Recrystallization of the substance of m.p. 185-187° gave needles of m.p. 186-188° (in a sealed capillary), the analysis of which corresponded to 5-(4-dimethylaminobutyl)-1-methyl-2(1H)-pyridone dihydrochloride. Found: C 51.24; 51.13; H 7.95; 7.92; Cl 24.72; 25.38%. $C_{12}H_{20}ON_2 \cdot 2HCl$. Calculated: C 51.24; H 7.79; Cl 25.27%.

In the usual way from 2 g of the hydrochloride we isolated the base as a colorless oil (1.0 g), which was vacuum-distilled at 2 mm: Fraction I (0.25 g), b.p. 167-169°; Fraction II (0.35 g), b.p. 170-170.5°; Fraction III (0.25 g), b.p. 171°. Analysis of Fraction II (colorless liquid, which darkened after one day): Found: C 69.31; 69.17; H 9.55; 9.60; N 13.43; 13.73%. $C_{12}H_{20}ON_2$. Calculated: C 68.23; H 9.62; N 13.46%. The analysis corresponds to the base (IX).

From an aqueous solution of the substance we isolated a picrate of m.p. 123-124°, raised to 124.5-125.5° by recrystallization from water. Found: C 43.26; 43.31; H 3.89; 3.89; N 16.36; 16.56%. $C_{24}H_{26}O_{15}N_8$. Calculated: C 43.24; H 3.90; N 16.82%. The analysis corresponds to 5-(4-dimethylaminobutyl)-1-methyl-2(1H)-pyridone dipicrate.

SUMMARY

1. By the hydrogenation of 1-methyl-5-(4-N-methylbenzamido-1-butenyl)-2(1H)-pyridone (IV; $R = COC_6H_5$), 1-methyl-5-(4-N-methylbenzamido-1-butenyl)-2(1H)-pyridone (VI) and 1-methyl-5-(4-N-methylbenzamido-1-butenyl)-2-piperidone (VII) were obtained.

2. When 1-methyl-5-(4-N-methylbenzamido-1-butenyl)-2-piperidone (VII) is boiled with hydrochloric acid, elimination of the benzoyl group is accompanied by opening of the piperidone ring with formation of 8-methylamino-4-(methylaminomethyl)octanoic acid, which under the action of alkali again undergoes ring closure with formation of 1-methyl-5-(4-methylaminobutyl)-2-piperidone (XII).

3. By the methylation of 1-methyl-5-(4-methylaminobutyl)-2(1H)-pyridone (VIII) and of 1-methyl-5-(4-methylaminobutyl)-2-piperidone (XII) we obtained 5-(4-dimethylaminobutyl)-1-methyl-2(1H)-pyridone (IX) and 5-(4-dimethylaminobutyl)-1-methyl-2-piperidone (XIII), respectively, and also their quaternary salts.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

KINETICS AND CHEMISTRY OF THE POLYCONDENSATION OF ESTERS OF α -AMINO ACIDS AND PEPTIDES

COMMUNICATION 12. POLYCONDENSATION OF GLYCYLGLYCINE ETHYL ESTER

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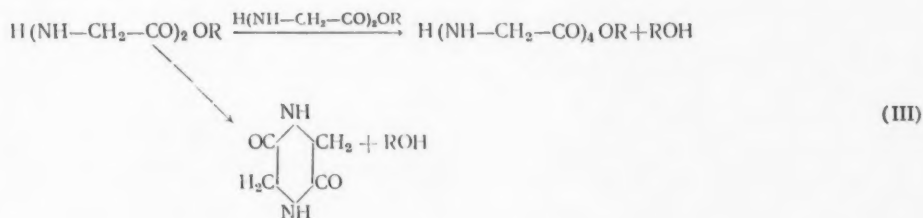
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In the polycondensation of dipeptide esters, together with linear peptides much piperazinedione is formed [1-3]. The readiness of the conversion into the piperazinedione is associated with the relatively high degree of free rotation around the α -carbon atoms in dipeptides and their derivatives. An intermediate stage in the condensation with formation of the piperazinedione is probably the isomeric transformation of the extended zig-zag form of the dipeptide into the curled-up form, which is stabilized by an intramolecular hydrogen bond $\text{—NH} \cdots \text{O}=\text{C} <$. The yields of tetrapeptide and of piperazinedione in the polycondensation of dipeptide esters may provide a measure of the relative concentrations of the extended and curled-up forms. The possibility of an equilibrium transformation of stereoisomeric forms of the dipeptide was proved by Mizushima and co-workers [4] by spectroscopic means for amides of acetamido acids (II), which are related to dipeptide esters (I):



Many investigations have been devoted recently to the polycondensation of tripeptides and still longer peptides with the object of obtaining macromolecular peptides having a direct alternation of amino acids [2, 5-7]. To obtain macromolecular peptides it was found to be necessary to use such severe conditions that, in addition to polycondensation, certain side reactions, mainly degradative processes, occurred [8, 9]. The degradation of esters of long peptides to dipeptides leads to the formation of a considerable amount of piperazinedione in the products of polycondensation [6, 9]. However, the study of the direct conversion of dipeptide esters into piperazinedione has not yet received adequate attention, in spite of the fact that this presents considerable interest for the investigation of systems containing dipeptide esters: the polycondensation of α -amino esters [10]; the polymerization of anhydrides of carboxyamino acids in presence of alcohols, alkoxides, and α -amino esters [11, 12]; the synthesis of peptides; etc.

In the present investigation we studied the kinetics of the change in the composition of the products of the polycondensation of glycylglycine ethyl ester in dioxane at 30°, 40°, 60°, and 80°. In all the experiments the initial concentration was 0.625 M. Chromatographic investigation in the course of the polycondensation showed that the transformation of the dipeptide ester proceeds in two directions; the condensation of two molecules of dipeptide results in the formation of the tetrapeptide ester, and intramolecular condensation gives piperazinedione; in both cases there is simultaneous liberation of ethanol.



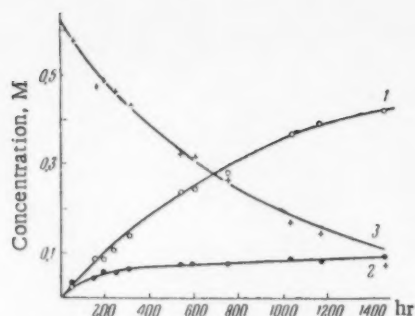


Fig. 1. Amount of glycyglycine ethyl ester consumed in formation of piperazinedione (1) and of tetrapeptide ester (2). Content of free dipeptide ester (3) in polycondensation of glycyglycine ethyl ester ($P_{20} = 0.625$; $t = 40$).

Rate Constants for the Conversion of Glycyglycine Ethyl Ester into Triglycyglycine Ethyl Ester (k_4) and Piperazinedione (k_D)

Temp. (°C)	$k_4 \cdot 10^{-7}$ ($\text{sec}^{-1} \cdot \text{mole}^{-1} \cdot \text{liter}$)	$k_D \cdot 10^{-7}$ (sec^{-1})
30	0,530	1,40
40	1,29	3,08
60	5,55	6,70
80	16,2	14,0

The formation of products of high molecular weight (hexapeptide and still longer peptides) requires relatively severe reaction conditions. At 80° the hexapeptide ester makes its appearance 150 hr after the start of the reaction, and at 60° only traces of the hexapeptide ester appear after 400 hr.

In the polycondensation products we could not detect the free peptides and their N-ethyl derivatives by means of paper chromatography. Hence, under our reaction conditions there was no migration of the alkyl group such as was observed by Slytermann [8] in the polycondensation of peptide esters under more severe conditions. The quantitative composition of the reaction products was determined on the basis of ethoxyl contents, and the tetrapeptide ester was determined by differential titration [13]. Data on the change in composition of the products of the polycondensation of glycyglycine ethyl ester in solution at 40° are given in Fig. 1. We showed previously [3] that in the polycondensation of glycyglycine in the solid state there is an induction period; moreover, additions of carbon dioxide and other acidic initiators for the polycondensation of α -amino esters have no effect on the length of the induction period and on the rate of polycondensation in a later period of the reaction. It will be seen from Fig. 1 that the polycondensation of glycyglycine ethyl ester in solution has no induction period, as a result of which it was relatively easy to measure the rate constants for the transformations of glycyglycine ethyl ester.

If we denote the molar concentrations of the piperazinedione and the dipeptide and tetrapeptide esters by D , P_2 and P_4 , respectively, then on the basis of the reaction scheme (III) we may write differential equations for the contents of these substances in the polycondensation product in the following form:

$$\frac{dP_4}{dt} = k_4 P_2^2 \quad (1)$$

$$\frac{dD}{dt} = k_D P_2 \quad (2)$$

$$\frac{dP_2}{dt} = k_D P_2 + k_4 P_2^2 \quad (3)$$

in which k_D and k_4 are rate constants of the conversion of glycyglycine into piperazinedione and the tetrapeptide, respectively. With the aid of Eqs. (1) and (2) these quantities were calculated graphically, and for experiments at 40° (Fig. 1) they were found to be: $k_4 = 1.29 \cdot 10^{-7} \text{ sec}^{-1} \cdot \text{mole}^{-1} \cdot \text{liter}$ and $k_D = 3.08 \cdot 10^{-7} \text{ sec}^{-1}$. In Fig. 1 the curve for the consumption of dipeptide ester was calculated by substituting the above rate constants in the solution of Eq. (3)

$$P_2 = \frac{P_{20}}{(x-1)e^{k_D D} - x}$$

in which the dimensionless quantity $x = \frac{k_4 P_{20}}{k_D} = 0.263$, and $P_{20} = 0.625$, the initial concentration of dipeptide ester.

In an analogous way we calculated the rate constants and the consumption curves for the dipeptide ester for series of experiments at 30°, 60°, and 80° (Table and Fig. 2).

From the data in the table and the Arrhenius equation we calculated the activation energies for the conversion of glycyglycine ethyl ester into piperazinedione and into the tetrapeptide ester (Fig. 3); they were found to be:

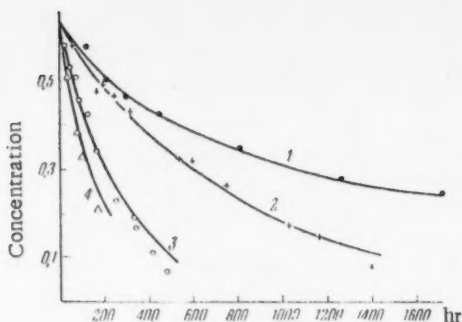


Fig. 2. Change in the content of glycylglycine ethyl ester during its polycondensation: 1) 30°; 2) 40°; 3) 60°; 4) 80°.

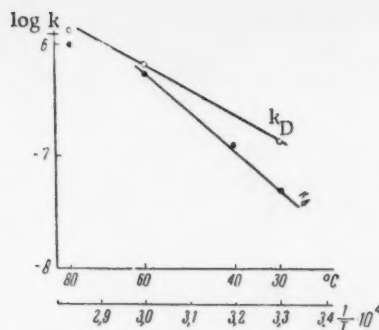


Fig. 3. Temperature-dependence of the rate constants for the formation of piperazinedione (k_D) and tetrapeptide ester (k_4).

$$\Delta E_D^* = 9.8 \text{ kcal/mole}$$

$$\Delta E_4^* = 14.0 \text{ kcal/mole}$$

These values of activation energy apply only in the range 30-60° because at 80° some side processes occur that are not described by the system of equations (1)-(3).

The polycondensation of peptide esters is essentially an ammonolysis of the esters. In fact, both in the values of the rate constants and in the activation energies obtained by us, the polycondensation of glycylglycine ethyl ester is close to the ammonolysis of esters under comparable conditions [14]. The ammonolysis of esters is speeded up appreciably under the action of additions of hydroxyl-containing compounds [15]. However, this catalytic acceleration is not so great that the liberation of alcohol in the polycondensation of glycylglycine in solution can have an appreciable effect on the course of the reaction. It might be expected, however, that the formation of alcohol would lead to some acceleration of the reaction in its later stages. Actually, as will be seen from Fig. 2, good agreement between the experimental results and the calculated curves for the consumption of dipeptide ester is observed in the early part of the reaction. When about one-half of the dipeptide taken in the experiment has reacted, it starts to be consumed somewhat faster than it should, according to the theoretical curve. In the polycondensation of the dipeptide ester in the solid state the liberation of alcohol may have a more pronounced accelerating effect because as well as the homogenization of the reaction mixture [3], a saturated solution of the dipeptide ester in alcohol is formed. It would be expected that in alcoholic solutions the polycondensation of dipeptide ester would be more rapid than in a neutral solvent such as dioxane, and we shall investigate this in the future.

Rees, Tong, and Young [7], who studied the polycondensation of a tripeptide ester (diglycylglycine methyl ester) in methanol, obtained results that differed from ours. The polycondensation of the tripeptide ester was about twenty times as rapid as the polycondensation of the dipeptide ester in dioxane. The activation energy for the polycondensation of diglycylglycine methyl ester was 5.5 kcal/mole. The authors explained such a low activation energy on the view that the condensation went through the stage of an intermediate complex consisting of two tripeptide molecules linked with two hydrogen bonds. In this case it would be expected that the experimentally measured polycondensation rate constant would fall with dilution, which the authors did not in fact observe. Such a marked lowering of the activation energy is probably associated with the peculiarities of the ammonolysis of esters in alcoholic solutions, for according to the results of Day, Gordon, and others [14, 16] the activation energy for the ammonolysis of methyl acetate in dioxane is lowered from 12.7 to 7.1 kcal/mole by the addition of considerable amounts (10 M) of alcohol. The formation of an intramolecular hydrogen bond in the curled-up configuration of the dipeptide ester may lead to a lowering of the activation energy for the formation of the peptide link. In fact, as shown in the present work, the activation energy for the formation of piperazinedione is about 4 kcal/mole less than that for the formation of the tetrapeptide. This difference in activation energy is approximately equal to the heat of formation of a hydrogen bond.

EXPERIMENTAL

Glycylglycine ethyl ester was prepared from its hydrochloride by Fischer's method and was crystallized twice from a mixture of chloroform and petroleum ether; m.p. 86°. Found: C 44.88; H 7.2; N 17.69%. $C_6H_{12}O_3N_2$. Calculated: C 45.00; H 7.5; N 17.50%. The literature [2] gives: m.p. 86°. Dioxane was purified and dried by Fieser's method.

The condensation was carried out in ampoules containing a definite weight of glycylglycine ethyl ester and a measured amount of dioxane. The ampoules were cooled, sealed, and placed in a thermostat, the temperature of which was kept constant within $\pm 0.05-0.1^\circ$. Four series of experiments were carried out at 30°, 40°, 60°, and 80°, respectively. The initial molar concentration of glycylglycine ethyl ester was 0.625. At this concentration the starting substance dissolved completely in dioxane in all experiments. During the reaction a precipitate formed in the solution. After definite intervals of time ampoules were opened and dioxane and alcohol were removed from the reaction mixture by vacuum distillation at room temperature. For the final removal of dioxane* we added a few milliliters of cyclohexane, which forms an azeotropic mixture with dioxane, and vacuum distillation was repeated. This operation was repeated several times. The residue was carefully ground and dried in a vacuum at a residual pressure of 1-2 mm. Control experiments carried out with solution of artificial mixtures of peptide esters and piperazinedione in dioxane and ethanol showed that this method of treating the reaction mixture ensures complete removal of dioxane and alcohol.

The product obtained after removal of solvent (the "dry residue") was analyzed. Its qualitative composition was studied by means of paper chromatography. The chromatograms were prepared on chromatographic paper "M" of the Leningrad No. 2 Factory in the system butyl alcohol-acetic acid-water (4 : 1 : 5). The chromatograms were treated by Reindell and Hoppe's method [17]. In the reaction products we detected diglycine ethyl ester, piperazinedione, the tetraglycine ethyl ester, and the hexaglycine ethyl ester ($R_F = 0.41, 0.30, 0.26$, and 0.19), which were identified by their R_F values [8]. The content of tetraglycine ethyl ester was determined by differential titration [13]. This method permits the determination of tetrapeptides only in absence of peptides of higher molecular weight. Since polycondensation at 80° was accompanied by the formation of the hexapeptide ester, tetraglycine was determined only in the initial period of this reaction in which chromatography showed the complete absence of hexapeptide ester. The ethoxyl content of the dry residue was determined by Viebock and Brecher's method. The amount of piperazinedione was calculated from the formula $c_D = 100 \cdot 1 - \frac{a + 0.117c_4}{28.1}$, in which a is the ethoxyl content (%), c_4 is the content of tetraglycine ethyl ester (%), and c_D is the piperazinedione content (%). The content of unchanged diglycine ester was calculated by difference. Taking account of the amount of ethanol liberated in the reaction we found the relations of the molar concentrations of all the components of the reaction mixture to time at 30°, 40°, 60°, and 80° (Figs. 1 and 2), which were used in the calculation of the rate constants.

SUMMARY

1. A study was made of the kinetics of the change in the composition of the products of the polycondensation of glycylglycine ethyl ester in dioxane.

2. The rate constants were measured, and the activation energies for the conversion of glycylglycine ethyl ester into tetraglycine ethyl ester and into piperazinedione were calculated.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE AND OLEFINS

COMMUNICATION 30. EFFECT OF THE PROPORTIONS OF THE COMPONENTS
OF THE ORIGINAL MIXTURE ON THE HYDROPOLYMERIZATION OF ISOBUTENE
UNDER THE CONJOINT ACTION OF HYDROGEN AND CARBON MONOXIDE

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As shown previously [1], at 190° under atmospheric pressure in presence of a Co catalyst [2] normal α -olefins readily undergo hydrocondensation with carbon monoxide and hydropolymerization in presence of small amounts of the latter. Both processes proceed with the participation of surface radicals formed by the reduction of carbon monoxide with hydrogen. The branched olefins trimethylethylene and tetramethylethylene scarcely react in this way. In absence of CO the hydropolymerization of olefins either scarcely occurs at all, as in the case of ethylene, or occurs only to a very small extent, this being the smaller the lower the molecular weight of the olefin.

However, isobutene stands apart from the other simple olefins in that it undergoes hydropolymerization under the same conditions under the action of hydrogen, but in absence of CO [3]. Isobutene again differs from the normal C_2 - C_6 olefins in that it polymerizes to some extent over a Co-clay catalyst in absence of CO and H_2 , and the addition of even very small amounts of H_2 (0.2%) doubles the yield of liquid polymerizate. The maximum yield of hydropolymerization products (up to 18% on the isobutene passed) is obtained with an equimolecular mixture of isobutene and hydrogen. It was found [4] that the addition of carbon monoxide to an isobutene-hydrogen mixture leads to a sharp rise in the yield of liquid hydrocarbons, which was found to be a maximum at a content in the original mixture of 2-4% CO and an isobutene : hydrogen ratio of two.

In the hydropolymerization of isobutene under the action of H_2 , but in absence of CO, the course of the reaction depends on the ratio of the amounts of reactants in the original mixture; at $i-C_4H_8 : H_2 = 3$ the products are mainly "true" polymers [5] having numbers of carbon atoms that are multiples of the number in the original isobutene, i.e., "diisobutene," "triisobutene," and their hydrogenation products. At $i-C_4H_8 : H_2 = 1$, after being fully hydrogenated the hydropolymerization products did not contain true hydropolymers, i.e., branched C_8 and C_{12} paraffins, and they consisted mainly of 2-methylalkanes, chiefly 2-methylbutane and 2-methylpentane. Such a composition indicates that the reaction has taken a new course, namely the destructure hydropolymerization of isobutene. It was shown previously [6] that under the same conditions an equimolecular mixture of isobutene and hydrogen containing 5-8% of CO gives a mixture of liquid hydrocarbons in which, after hydrogenation, 2-methylalkanes were again found and were predominant in the C_5 - C_8 fractions.

Our object in the present work was to investigate the relation of hydropolymerization of isobutene under the same conditions to the CO content and the $i-C_4H_8 : H_2$ ratio in the ternary mixture $i-C_4H_8-H_2-CO$.

EXPERIMENTAL

The apparatus, the method of preparing the original gases, and the experimental procedure did not differ from those used previously [7]. We used a precipitated Co-clay catalyst [2] which has been customarily used in work on the hydrocondensation of CO with olefins and the hydropolymerization of the latter under the action of small amounts of CO [1]. The glass reaction tube, diameter 10 mm, was filled with 30 ml of catalyst, which was regenerated after every 15-20 hr of work. The reaction was carried out under atmospheric pressure at 190° with a space velocity of the original gas of about 100 hr^{-1} . In prolonged experiments with gas mixtures of definite composition we obtained

TABLE 1. Compositions of Original Mixtures and Properties of Hydropolymerizates Obtained

Original mixture			Hydropolymerizate				Hydropolymerizate after hydrogenation		
No.	i-C ₄ H ₈ : H ₂	CO (%)	d ₄ ²⁰	n _D ²⁰	bromine value	content of unsaturateds (%)	d ₄ ²⁰	n _D ²⁰	amt. of fractionated (ml)
1	1	0	0,6432	1,3870	46,4	29	0,6398	1,3752	28
2	1	1	—	—	26,0	16	0,6683	1,3872	25
3	1	5	0,6735	1,3934	56,6	35	0,6712	1,3890	68
4	1	7	—	1,3988	85,2	53	0,6820	1,3964	32
5	1	20	—	1,4122	93,5	66	0,7083	1,4074	31
6	2	5	0,6902	1,3986	73,2	52	0,6846	1,3960	72
7	3	0	—	1,4083	111,3	78	0,6909	1,3979	100
8	3	4	0,7010	1,4142	149,0	100	0,6972	1,4015	82

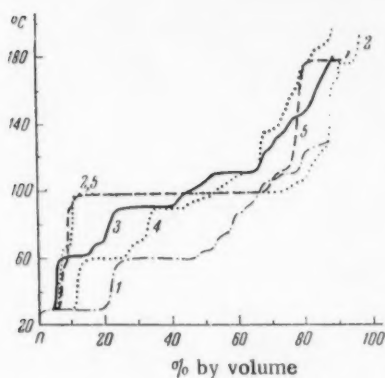


Fig. 1. Fractionation curves of hydrogenated hydropolymerizates: 1) Mixture 1; 2) mixture 7; 3) mixture 3; 4) mixture 6; 5) mixture 8.

considerable amounts (50-100 ml) of liquid hydropolymerizates, which after separation from reaction water and drying, were freed from C₄H₆ and C₄H₁₀ and then hydrogenated at room temperature over platinized charcoal with an addition of H₂PtCl₆ [8]. The resulting hydrogenation products of zero bromine value were fractionated through a column with a filling of triangular copper spirals and of 40-plate efficiency up to a temperature of 125-130°, and the residues were further distilled from a Wurtz flask.

Table 1 gives the compositions of the original gas mixtures expressed as the volume ratio i-C₄H₈ : H₂, which was varied in the range of 1-3, and the CO content, which was varied from zero to 20%. In the same Table 1 we give the constants of the liquid hydropolymerizates obtained (after debutanization), and also the volumes taken for the fractionation and the constants of the hydropolymerizates after complete hydrogenation. It will be seen from Table 1 that with rise in the CO content of the original mixture the amount of unsaturated hydrocarbons in the hydropolymerizate usually rises, which follows from a comparison of the results obtained with Mixtures 1-5 and also 7-8; there is a simultaneous rise in the values of d₄²⁰ and n_D²⁰ of the hydrogenated catalyzates, which indicates a rise in the content of hydrocarbons of high molecular weight; there will be further confirmation of this below.

Figures 1 and 2 give the fractionation curves of the hydrogenation products, and Tables 2-9 give the main fractions obtained; these consist of separate hydrocarbons corresponding to plateaux on the fractionation curves and having constants coinciding with or extremely close to data in the literature [9] (Table 10). Tables 2-9 give also large over-all fractions consisting of mixtures of hydrocarbons which have not been separated in the fractionation.

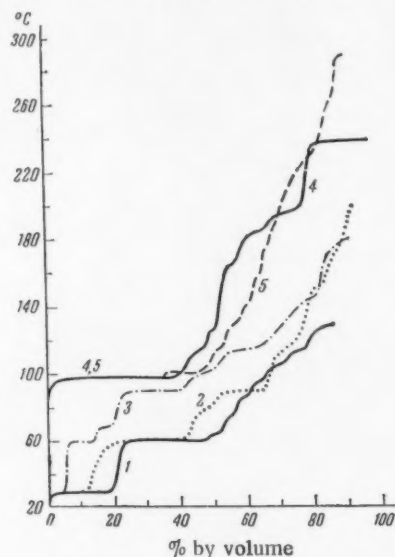


Fig. 2. Fractionation curves of hydrogenated hydropolymerizates: 1) Mixture 1; 2) mixture 2; 3) mixture 3; 4) mixture 4; 5) mixture 5.

TABLE 2. $i\text{-C}_4\text{H}_8 : \text{H}_2 = 1$; 0% CO

Fraction	Boiling range	Yield (% by vol.)	n_D^{20}	d_4^{20}	Hydrocarbon
I	27,5—28	20,0	1,3540	0,6202	2-Methylbutane
III	60—61,0	29,8	1,3710	0,6528	2-Methylpentane
IV	61—99	17,1	1,3819	0,6802	
V	99—126	18,2	1,3978	0,7062	
Residue	> 126	7,2	1,4078	—	

TABLE 3. $i\text{-C}_4\text{H}_8 : \text{H}_2 = 1$; 1% CO

Fraction	Boiling range	Yield (% by vol.)	n_D^{20}	d_4^{20}	Hydrocarbon
I	27—28	13,2	1,3540	0,6198	2-Methylbutane
III	60—61	27,0	1,3715	0,6531	2-Methylpentane
V	90—90,5	12,9	1,3852	0,6791	2-Methylhexane
VI	90,5—125	11,3	1,3939	0,6955	
VII	125—218	17,4	1,4160	0,7409	

TABLE 4. $i\text{-C}_4\text{H}_8 : \text{H}_2 = 1$; 5% CO

Fraction	Boiling range	Yield (% by vol.)	n_D^{20}	d_4^{20}	Hydrocarbon
I	28—29,5	6,2	1,3536	—	2-Methylbutane
III	60,5—61,0	8,5	1,3717	0,6530	2-Methylpentane
IV	61—90,0	11,2	1,3808	0,6749	
V	90—91,0	15,0	1,3852	0,6789	2-Methylhexane
VI—VII	91—116	10,2	—	—	
VIII	116—118	10,0	1,3958	0,6981	2-Methylheptane
IX—X	118—178	26,1	—	—	
Residue	> 178	7,6	1,4325	—	

For brevity, in these tables we do not give intermediate fractions isolated in low yield and having no determining significance for the determination of the compositions of the hydropolymerizates. In Table 11 for the series of mixtures 1-5 we give the yields of liquid hydrocarbons, the degrees of conversion of the separate components, and the proportions in which they entered the reaction of formation of liquid hydrocarbons (during the first five hours and the subsequent five hours).

Effect of the $i\text{-C}_4\text{H}_8 : \text{H}_2$ ratio in the original mixture on the composition of the hydropolymerizate. To resolve this question we shall compare results obtained with mixtures of identical CO content. Such mixtures are Mixture 1 (Table 2, Fig. 1, Curve 1) and 7 (Table 8; Fig. 1, Curve 2) in which the CO content is zero and the $i\text{-C}_4\text{H}_8 : \text{H}_2$ ratios are 1 and 3, respectively; also Mixtures 3 (Table 4; Fig. 1, Curve 3), 6 (Table 7; Fig. 1, Curve 4), and 8 (Table 9; Fig. 1, Curve 5) with a CO content of 4-5% and $i\text{-C}_4\text{H}_8 : \text{H}_2$ ratios of 1, 2, and 3, respectively. From a comparison of the data in Tables 2 and 8 and Curves 1 and 2 (Fig. 1) it will be seen that with $i\text{-C}_4\text{H}_8 : \text{H}_2 = 1$ and in absence of CO the hydrogenation product contains 20% of 2-methylbutane and about 30% of 2-methylpentane. Moreover, on the fractionation curve (Fig. 1, Curve 1) there are arrests at 90-91° and 114-115°, which probably correspond to 2-methylhexane and 2-methylpentane. With $i\text{-C}_4\text{H}_8 : \text{H}_2 = 3$ the hydrogenation product contains 64% of 2,2,4-trimethylpentane and about 5% of dodecane isomers, but only 4% of 2-methylbutane and 2.5% of 2-methylpentane. Hence, in the first case only destructive hydropolymerization of isobutene occurs, and in the second, there is mainly true polymerization, though there is also some destructive polymerization, but only a little. On comparison of Tables 4, 7, and 9 and Curves 3-5 (Fig. 1) it is seen that an addition of 4-5% of CO does not essentially affect the main course of the reaction, as observed in absence of CO for a definite $i\text{-C}_4\text{H}_8 : \text{H}_2$ ratio. Actually, when $i\text{-C}_4\text{H}_8 : \text{H}_2 = 1$ (Table 4), the hydrogenation product contains products of the destructive hydropolymerization of isobutene, but there is a greater selection of 2-methylalkanes, starting from 2-methylbutane and ending with

TABLE 5. $i\text{-C}_4\text{H}_8 : \text{H}_2 = 1$; 7% CO

Fraction	Boiling range	Yield (% by vol.)	n_D^{20}	d_4^{20}	Hydrocarbon
II	49—50	6,9	1,3682	0,6488	2,2-Dimethylbutane
IV	60—60,5	8,7	1,3712	0,6530	2-Methylpentane
VI	69—70	3,0	1,3774	—	Hexane
VIII	90—90,5	10,5	1,3854	0,6788	2-Methylhexane
X	97—99	6,3	1,3905	0,6851	Heptane and 2,2,4-trimethylpentane
XII	101—130	13,7	1,3964	0,7031	2-Methylheptane and octane
XIII—XV	130—236	45,2	—	—	

TABLE 6. $i\text{-C}_4\text{H}_8 : \text{H}_2 = 1$; 20% CO

Fraction	Boiling range	Yield (% by vol.)	n_D^{20}	d_4^{20}	Hydrocarbon
I	85,5—98,0	1,3	1,3865	—	
II	98,0—98,5	33,0	1,3879	0,6839	Heptane
III	98,5—99,0	13,8	1,3900	0,6873	2,2,4-Trimethylpentane
V—VI	107—137	10,6	—	—	
VII—VIII	137—290	27,6	—	—	
Residue	>290	5,9	1,4380	—	

TABLE 7. $i\text{-C}_4\text{H}_8 : \text{H}_2 = 2$; 5% CO

Fraction	Boiling range	Yield (% by vol.)	n_D^{20}	d_4^{20}	Hydrocarbon
I	27,0—29,0	9,6	1,3540	0,6201	2-Methylbutane
III	60—60,5	10,5	1,3718	0,6536	2-Methylpentane
V	89,5—90,5	7,0	1,3854	0,6789	2-Methylhexane
VII	96,0—98,6	7,8	1,3880	0,6854	Heptane
IX	116,5—119,0	5,4	1,3954	0,6982	2-Methylheptane
X—XII	119—189	24,5	—	—	
Residue	>189	5,6	1,4305	—	

2-methylheptane. These results confirm those obtained earlier [6]. When $i\text{-C}_4\text{H}_8 : \text{H}_2$ (Table 7), the hydrogenation product again consists mainly of 2-methylalkanes, but also contains 7.8% of heptane. In these hydrogenation products the hydrodimer of isobutene is quite absent. When $i\text{-C}_4\text{H}_8 : \text{H}_2 = 3$ (Table 9), the hydrogenation product contains mainly hydrodimer (52.5%) and hydrotrimer (about 12%) with only about 6% of 2-methylbutane.

Effect of the carbon monoxide content of the original mixture on the composition of the hydropolymerizate. The results given in the preceding section already indicate some changes produced in the compositions of the hydropolymerizates by the addition of CO to the original mixture. To obtain a more accurate picture of this question we shall compare results obtained with mixtures having a constant $i\text{-C}_4\text{H}_8 : \text{H}_2$ ratio but different CO contents. Here we have the series consisting of Mixtures 7 (Table 8; Fig. 1, Curve 2) and 8 (Table 9; Fig. 1, Curve 5) and another series consisting of Mixtures 1 (Table 2; Fig. 2, Curve 1), 2 (Table 3; Fig. 2, Curve 2), 3 (Table 4; Fig. 2, Curve 3), 4 (Table 5; Fig. 2, Curve 4), and 5 (Table 6; Fig. 2, Curve 5). In the first series $i\text{-C}_4\text{H}_8 : \text{H}_2 = 3$, and in absence of CO the true polymerization of isobutene occurred. The course of the reaction was not changed by the addition of 4% of CO, but the latter caused a shift in the direction of the formation of compounds of higher molecular weight. The content of hydrodimer fell from 64% to 52.5%, and that of hydrotrimers rose from 4.7% to 11.7%. The 2-methylalkane content remained low, as before (Tables 8 and 9; Fig. 1, Curves 2 and 5). In the other series of mixtures the CO content varied from zero to 20% and $i\text{-C}_4\text{H}_8 : \text{H}_2 = 1$. As stated above, with $i\text{-C}_4\text{H}_8 : \text{H}_2 = 1$ in absence of CO mainly destructure hydropolymerization of isobutene occurs with formation of a reaction product that contains

TABLE 8. $i\text{-C}_4\text{H}_8 : \text{H}_2 = 3$; 0% CO

Fraction	Boiling range	Yield (% by vol.)	n_D^{20}	d_4^{20}	Hydrocarbon
II	27,5—28	4,0	1,3540	0,6205	2-Methylbutane
IV	63—65	2,5	1,3731	0,6546	2-Methylpentane
VI	98,5—99,5	64,2	1,3315	0,6922	2,2,4-Trimethylpentane
VII—X	99,5—177	14,3	—	—	$\text{C}_{12}\text{H}_{26}$
XI—XII	177—188	4,7	—	—	
XIII	188—195	4,4	—	—	

TABLE 9. $i\text{-C}_4\text{H}_8 : \text{H}_2 = 3$; 4% CO

Fraction	Boiling range	Yield (% by vol.)	n_D^{20}	d_4^{20}	Hydrocarbon
II	27—28	5,8	1,3530	0,6186	2-Methylbutane
IV—V	54,5—98,5	11,3	—	—	
VI	98,5—99	52,5	1,3917	0,6906	2,2,4-Trimethylpentane
VII—VIII	99—175	8,8	—	—	$\text{C}_{12}\text{H}_{26}$
IX	175—180	11,7	1,4277	0,7537	
Residue	>180	6,4	1,4392	0,7806	

TABLE 10. Data in Literature [9] for Constants of Hydrocarbons Found in Hydrogenation Products of Hypopolymerizates

Fraction	B.p. ($^{\circ}\text{C}$ at 760 mm)	d_4^{20}	n_D^{20}
2-Methylbutane	27,85	0,6197	1,3537
2,2-Dimethylbutane	49,74	0,6492	1,3688
2-Methylpentane	60,27	0,6532	1,3715
Hexane	68,7	0,6594	1,3749
2-Methylhexane	90,05	0,6786	1,3849
Hexane	98,43	0,6837	1,3877
2,2,4-Trimethylpentane	99,24	0,6919	1,3915
2-Methylheptane	117,65	0,6979	1,3950
Octane	125,67	0,7025	1,3974

2-methylalkanes after hydrogenation. On addition of up to 5% of CO to the original equimolecular isobutene-hydrogen mixture, the same reaction occurs with increase in the relative yields of the higher 2-methylalkanes. With increase in the CO concentration to 7%, normal paraffins (hexane, heptane, octane), isobutene hydrodimer, and also small amounts of 2,2-dimethylbutane make their appearance in the hydrogenated reaction product. When the CO content is 20% 2-methylalkanes disappear from the hydrogenation product and up to 14% of 2,2,4-trimethylpentane appears. It is of particular interest that with 20% of CO in the original gas the hydrogenated catalyzate begins to boil relatively high and $\text{C}_5\text{--C}_6$ hydrocarbons are completely absent, though it contains 33% of heptane. It may be noted that in experiments with Mixture 6 we also found up to 8% of heptane apart from 2-methylalkanes. Fig. 3 shows the relation of the contents of various hydrocarbons and also the total amount of 2-methylalkanes in the hydrogenated catalyzates to the CO concentration in the original mixture. With rise in the CO concentration there is a fall in the total content of 2-methylalkanes and, in particular, of 2-methylbutane and 2-methylpentane. On the curves the 2-methylhexane and 2-methylheptane contents show maxima. With rise in the CO content from 7% to 20% there is a rise in the amounts of 2,2,4-trimethylpentane and particularly of heptane.

The destructive hypopolymerization of isobutene, which occurs with $i\text{-C}_4\text{H}_8 : \text{H}_2$ ratios of 1-2 (35-50% H_2) and CO concentrations not exceeding 5%, probably has a free-radical-chain character; for one CO molecule entering into the formation of liquid hydrocarbons, 5-18 isobutene molecules are drawn into this reaction. At higher CO

TABLE 11. Effect of the Molar Proportions of Components in the Original Gas Mixture on the Yield of Liquid Polymerizate; the Proportions of the Components that React, and the Molar Proportions of Components Consumed in the Formation of Liquid Hydrocarbons

Mixture No.	Molar proportions CO : H ₂ : i-C ₄ H ₈ in original mixture	Yield of liquid hydrocarbons		Amt. that reacts (% on original)			Molar proportions CO : H ₂ : i-C ₄ H ₈ consumed in formation of liquid hydrocarbons
		% on original isobutene	% on isobutene that reacts	iso-butene	CO	H ₂	
1	0 : 1 : 1	16,0	18,4	86,8	—	81,0	0 : 1,3 : 1
1	0 : 1 : 1	6,8	7,7	88,3	—	100,0	0 : 3,3 : 1
2	1 : 40 : 40	50,5	60,0	84,0	100,0	94,5	1 : 19,1 : 17,7
2	1 : 40 : 40	48,8	62,5	78,1	77,4	96,0	1 : 25,0 : 14,7
3	1 : 9,5 : 9,5	58,3	67,0	87,0	100,0	67,5	1 : 7,0 : 8,7
3	1 : 9,5 : 9,5	47,0	65,5	71,7	77,3	84,0	1 : 8,1 : 5,2
4	1 : 6,6 : 6,6	49,7	45,3	43,5	77,4	75,0	1 : 3,9 : 0,7
4	1 : 6,6 : 6,6	19,9	51,0	39,0	88,5	70,0	1 : 3,8 : 1,2
5	1 : 2 : 2	10,2	34,0	29,8	77,6	47	1 : 0,5 : 0,1

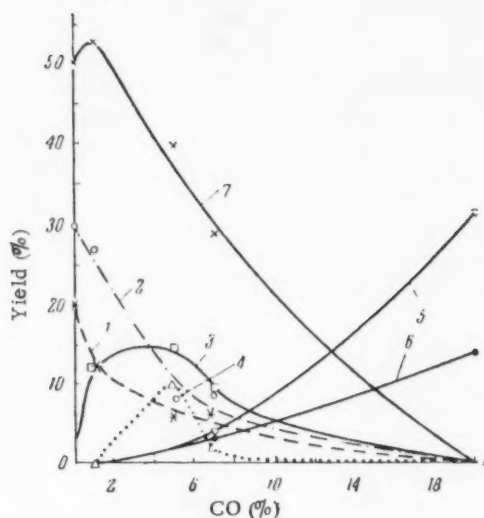


Fig. 3. Relation of the yields of individual hydrocarbons to the carbon monoxide content of the original gas mixture: 1) 2-methylbutane; 2) 2-methylpentane; 3) 2-methylhexane; 4) 2-methylheptane; 5) heptane; 6) 2,2,4-trimethylpentane; 7) total 2-methylalkanes.

the destructive hydrogenation of isobutene itself, as a result of which reactive alkyl radicals are formed which then react with undecomposed isobutene molecules with the formation of 2-methylalkanes and the corresponding olefins. Processes of destructive hydrogenation of isobutene will proceed with greater intensity and to a greater extent the higher the hydrogen concentration on the catalyst surface, and this will clearly fall with increase in the CO and i-C₄H₈ contents of the original gas.

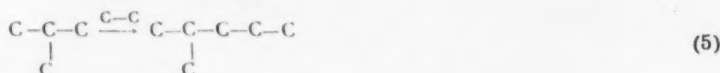
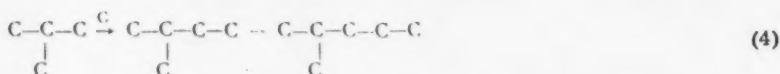
Diagrammatically these processes can be represented as follows, arranging them in order of increased extent of breakdown:



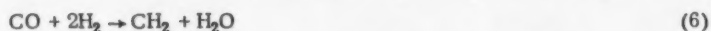
concentrations a different relation is observed; at 7% of CO, for one CO molecule about one isobutene molecule is brought into reaction, and at 20% of CO only 0.1 of an isobutene molecule reacts; there is a simultaneous fall in the yield of liquid hydrocarbons on the amount of isobutene passed (Table 11). In this CO concentration range the destructive hydropolymerization of isobutene is weakened at the expense of its true polymerization and the Orlov-Fischer-Tropsch reaction. The latter is particularly intense at 20% of CO in the original mixture. An examination of the results shows that at high values of i-C₄H₈ : H₂ there predominate processes of true polymerization of isobutene, whereas with diminution in this ratio the part played by the destructive hydropolymerization of isobutene increases if the CO content of the original mixture does not exceed 5%.

On the basis of the experimental results obtained earlier [4, 10] it was concluded that the products of the destructive hydropolymerization of isobutene cannot be formed by the degradation of 2,4,4-trimethyl-1-pentene under the action of hydrogen. This conclusion follows also from some of the results obtained in the present work. Actually, it is impossible to explain the formation of 2-methylhexane or 2-methylheptane and the corresponding olefins by the direct degradation of 2,4,4-trimethyl-1-pentene or its hydrogenation product. It may be supposed that in the destructive hydropolymerization of isobutene the primary reaction is

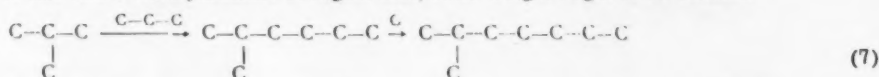
As the CO content of the original gas and the value of $i\text{-C}_4\text{H}_8 : \text{H}_2$ increases, process (1) will become more intense and process (3) will weaken. Thus, in absence of CO with a $i\text{-C}_4\text{H}_8 : \text{H}_2$ ratio of 1-2 the degradation of isobutene leads mainly to the formation of radicals with one, and to a less extent two, carbon atoms. Reaction may proceed further by the following scheme:



Under these conditions mainly 2-methylbutane and 2-methylpentane and the corresponding olefins are in fact formed. On addition of small amounts of CO, this also forms radicals with one carbon atom, probably as in the reaction



Also, with addition of CO the breakdown of isobutene by Reaction (1) is intensified. For this reason the yield of liquid hydrocarbons begins to rise and 2-methylalkanes of higher molecular weight begin to be formed:



With higher amounts of CO in the original gas the breakdown of isobutene evidently goes exclusively by Reaction (1), but a considerable number of radicals with one C atom are formed as a result of the hydrogenation of carbon monoxide. However, under these conditions there are few isobutene molecules on the catalyst surface with which these radicals could react. They therefore react among themselves and effect Orlov-Fischer-Tropsch synthesis. The presence of a considerable number of radicals with three carbon atoms, formed by Scheme (1), results in their combination with formation of hexane and in presence of a large numbers of CH_2 radicals it leads also to the formation of heptane. The latter may be formed by the bridge scheme:



which was suggested earlier [11]. In this way the formation of various hydrocarbons obtained in our experiments may be explained.

SUMMARY

1. An investigation was made of the dependence of the course of the hydropolymerization of isobutene under the action of CO and H_2 on the proportions of the components of the original $i\text{-C}_4\text{H}_8\text{-H}_2\text{-CO}$ mixture.
2. With a CO content of the original mixture of up to 5% and an $i\text{-C}_4\text{H}_8 : \text{H}_2$ ratio of 1-2 there mainly occurs destructive hydropolymerization of isobutene with formation of 2-methylalkanes and the corresponding olefins, but at $i\text{-C}_4\text{H}_8 : \text{H}_2 = 3$ there occurs true polymerization of isobutene with formation of dimers, trimers, and their hydrogenation products.
3. In the CO concentration range 7-20% Orlov-Fischer-Tropsch synthesis predominates. There is preferential formation of n-heptane and also of isobutene dimers.
4. Possible schemes for the formation of the hydrocarbons obtained are examined.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

REACTIONS IN THE CATALYTIC HYDROGENATION
OF ORGANIC COMPOUNDS CONTAINING
A QUATERNARY CARBON ATOM

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The catalytic hydrogenation of "isooctane,"* which contains a quaternary carbon atom, in the range 360-510° has been described in the literature. The primary transformation of "isooctane" was effected mainly by cleavage of the molecule at a bond of the quaternary carbon atom with formation of two molecules of isobutane, and it proceeded considerably more rapidly than the breakdown of normal paraffins of the same molecular weight.

According to Pier's result [1], at a given temperature under autoclave conditions (pressure about 200 atm) "isooctane" decomposes over tungsten sulfide about twenty times as fast as heptane with formation of almost pure isobutane. In a flow apparatus at 400° and 250 atm with a space velocity of 1.5 hr⁻¹, the conversion of the "isooctane" was about 40%. The conversion of "isooctane" over a commercial WS₂ + aluminum silicate catalyst at 360° and 300 atm. with a space velocity of 1.5 hr⁻¹ is, as Zakharenko showed [2], 70%, and more than 90% of the decomposition products are the result of the breakdown of the "isooctane" into two molecules of isobutane. Analogous results were obtained by Lozovoi and Tserlina [3] and by Lozovoi, Senyavin, and Sovetova [4] at 510° and 75-300 atm over a commercial alumina-molybdena catalyst and a catalyst based on aluminum silicate.

In catalytic cracking over a zirconia-aluminum silicate catalyst similar in its activity to commercial catalysts, not increase in the rate of breakdown of isooctane, as compared with n-octane, was observed, but the total conversions of these compounds at 550° with a space velocity of 1.2 hr⁻¹ and with a duration of the process of 30 min were 49% and 42%, respectively [5].

Preferential cleavage at the bond formed by a quaternary carbon atom with the benzene ring was observed by Moldavskii and Bezdel' [6] in the catalytic cracking of alkylbenzenes; they observed also a weakening of this bond when there was a methyl substituent in the benzene ring. Under the given conditions (410°, space velocity 1.5 hr⁻¹, activated gumbrim) butylbenzene did not decompose, whereas with t-butylbenzene the elimination of butene occurred to the extent of 67%, with m-t-butyltoluene it occurred to the extent of 86%, and with p-t-butyltoluene elimination was almost complete. According to Greensfelder, Voge, and Good, in catalytic cracking at 400° with a space velocity of 12.5 moles · liter⁻¹ · hr⁻¹ the extents of the dealkylation of C₄-alkylated benzenes are: n-butylbenzene 14%, s-butylbenzene 50%, and t-butylbenzene 80% [5].

In a patent of Luten and Good [7] it is proposed to dealkylate t-butylcresols and t-butylxylenols at 250-550° (preferably 350-400°) at a space velocity of 0.1-20 hr⁻¹. The degree of dealkylation was not stated. Stevens [8] attained complete dealkylation of t-butylcresols and t-butylxylenols under the action of 95% sulfuric acid taken in an amount of 0.5-2% on the weight of raw material at a temperature of 202° for one hour.

In the present work we have observed that the presence of a hydroxy substituent in the benzene ring greatly weakens the bond between the ring and a quaternary carbon atom, and under the conditions of hydrogenation at very low temperatures this results in selective, almost quantitative breakdown of the molecule at this carbon-carbon bond.

EXPERIMENTAL

As model organic compounds we took p-α,α-dimethylbenzylphenol (C 85.27; H 7.64%; O 7.09%; mol. wt. 218; m.p. 67-68°; calculated values: C 85.00%; H 7.64%; O 7.36%; mol. wt. 212), 4,4'-isopropylidenediphenol (C 78.66%;

*The term "isooctane" here clearly refers to 2,2,4-trimethylpentane.—Publisher.

Compositions of Hydrogenation Products

Starting compounds	p- α , α -Dimethylbenzylphenol	4,4'-Isopropylidene diphenol
	Yield (%) by wt.)	Yield (%) by wt.)
Methane	0.8	0.2
Propane	—	4.2
Water	0.5	0.9
Toluene	2.5	0.8
Cumene	47.8(51.4)*	—
Phenol	41.0(40.4)*	46.4(37.6)*
Isopropylphenol	—	41.0(54.5)*
2,2-Diphenylpropane	5.0	4.0
p- α , α -Dimethylbenzylphenol	3.4	—
4,4'-Isopropylidenediphenol	—	3.6**
Total	101.0	101.0
Consumption of hydrogen	1.0	1.0
Gas and losses in discharging	1.4	1.5
Losses in fractionation	0.4	0.6

*In parenthesis we give the theoretical yield for the experimentally attained degree of conversion for the stage of the breakdown of the original molecule only at the bond with the quaternary carbon atom.

**On the assumption of equal concentrations of the two compounds.

H 7.11%; O 14.23%; mol. wt. 221; m.p. 151-153°; calculated values: C 78.80%; H 7.02%; O 14.18%; mol. wt. 228), and "isooctane" [2,2,4-trimethylpentane] (d_4^{20} 0.6925, n_D^{20} 1.3928; b.p. 99.3°; the literature gives: d_4^{20} 0.6918; n_D^{20} 1.3916; b.p. 99.3°). The experiments were carried out in a two-liter rotating autoclave, which was charged with 200 g of the starting substance and 100 cc of industrial WS_2 + NiS + Al_2O_3 catalyst* (in the experiment with 4,4'-isopropylidenediphenol 200 cc of catalyst was taken); the temperature was 275°, the initial hydrogen pressure 40 atm, and the duration was 30 min (the time taken in the preliminary heating was about 50 min). The autoclave was cooled, gas was allowed to escape, and the contents were discharged and weighed. The liquid hydrogenation product was filtered from catalyst, and the small amount of liquid products left on the latter was distilled off in a flask. The combined liquid products were fractionated through a column of about 40-plate efficiency with collection of suitable narrow fractions, which were identified by their boiling ranges, refractive indices, states of aggregation, chromatographic separation, the gravimetric determination of phenol content, and the infrared spectra. The gas formation and consumption of hydrogen in the hydrogenation were calculated on the basis of the material balance and the individual composition of the hydrogenation product. Losses in the discharging and fractionation of the hydrogenation product were only slight (table), and were distributed in accordance with the yields of the products.

DISCUSSION OF EXPERIMENTAL RESULTS

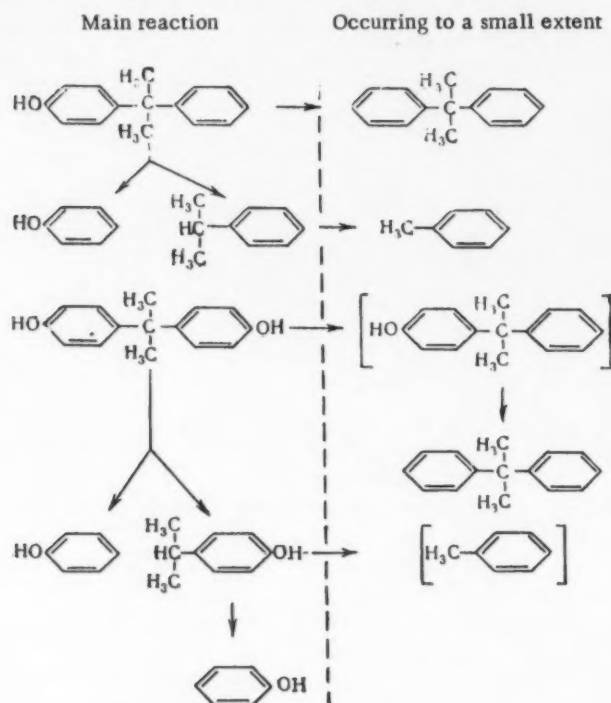
The table gives the individual compositions of the hydrogenation products from p- α , α -dimethylbenzylphenol and 4,4'-isopropylidenediphenol. On the basis of the results obtained a scheme is given which shows the proposed mechanism of the transformations undergone by these compounds under the given conditions; the structure of components shown in brackets have not been completely proved, but their probable correctness follows from the structure of the starting compound and the experimental results. The "isooctane" did not undergo any transformations,

*As a result of long storage the sample of catalyst used had partially lost its original hydrogenation activity.

since the hydrogenation product (100% yield on the weight taken) scarcely differed from the original "isooctane": d_4^{20} 0.6920; n_D^{20} 1.3923; b.p. 99.3°.

An examination of the results brings to light some peculiar features of the transformations of the organic compounds containing a quaternary carbon atom. At the very low hydrogenation temperature of 275° there is a high-yield (91 mole per cent) selective breakdown of p- α , α -dimethylbenzylphenol at a bond of the quaternary carbon atom with formation of phenol and cumene as primary reaction products. It is characteristic that isopropylphenol and benzene are absent from the hydrogenation product.

Scheme of Transformations in the Hydrogenation of Organic Compounds Having a Quaternary Carbon Atom (Temperature 275°)



This indicates the great weakening of the bond of the quaternary carbon atom with the hydroxyphenyl group as compared with its bond with the phenyl group. A secondary reaction occurs to a slight extent: the breakdown of cumene to toluene* (5.3 moles per cent) and also the reduction of the original phenol (3.4 moles per cent).

A similar picture is observed in the case of the hydrogenation of 4,4'-isopropylidenediphenol,* the primary breakdown of which proceeds to the extent of 91.8 moles per cent with formation of phenol and isopropylphenol, with this difference that the latter undergoes further breakdown at the bond between the tertiary carbon atom and the hydroxyphenyl group (about 25 moles per cent on the isopropylphenol formed) to a much greater extent than cumene did in the preceding experiment (about 6 moles per cent on the cumene formed). As stated above, "isooctane" was found to be stable under the experimental conditions, so that a carbon-carbon bond between a quaternary carbon atom and an aliphatic chain was stable.

Thus, the experimental results given above enable us to establish the existence of an extremely interesting phenomenon: a great reduction of the stability of a carbon-carbon bond between an aliphatic chain and a benzene ring under the influence of a phenolic hydroxyl in the ring (in our case in the para position). The greatest reduction

*When the temperature is lowered to 250° and the duration of the experiment is reduced to five minutes, the formation of toluene is not observed.

in the stability of the carbon-carbon bond occurs when there is a quaternary atom in the aliphatic chain; the reduction is less for a tertiary atom; and it may be supposed it will be still less for the bond of a secondary carbon atom with a hydroxyphenyl group. It is possible that this fact is of no little importance for the acceleration of decomposition reactions in the liquid-phase destructive hydrogenation of the complex matter of coals and heavy resinous residues which contain hydroxyphenyl groups.

SUMMARY

It was shown that under hydrogenation conditions in presence of a tungsten sulfide catalyst there is a great weakening of the bond formed by a quaternary carbon atom with a benzene ring under the influence of a p-hydroxyl in the latter, and this brings about high-yield selective breakdown of the molecule of the organic compound.

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THE BURNING OF SECONDARY HIGH EXPLOSIVES UNDER HIGH PRESSURE UP TO 1000 kg/cm²

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In order to utilize high explosives efficiently it is necessary to study their properties under different conditions. The investigation of the relation between the burning velocity and pressure is of special importance since it is one of the basic physical factors which determines the conditions of the burning process. At low pressures—from 2 kg per cm² and lower—this relation has been studied in comparative detail. Under these conditions a number of secondary high explosives [1-3] and initiating high explosives [4-6] give a linear relation between the burning velocity U and the pressure P described by the equation

$$U = A + BP \quad (1)$$

where U is the burning velocity; P is the pressure; A is the velocity component independent of pressure. In certain cases a deviation from this law has been observed in the direction of a large increase in the burning velocity with increase of P . Certain authors have explained the pressure of the constant "A" in the equation when initiating high explosives are used, by the possibility that burning occurs in the condensed phase at an increased pressure in comparison with the external pressure.

We examined the effect of high pressures on the burning of a series of solid and liquid high explosives in a series of investigations. In this article we are briefly reporting the results of our observations on the burning of hexogene and penthrite in an atmosphere of nitrogen at a pressure of up to 1000 kg/cm². In order to carry out these investigations we designed an apparatus which permitted the tests to be conducted at a static gas pressure of up to 2000 kg/cm². The bombs were supplied with longitudinal and curved windows for photographing the process and with the requisite number of leads for the thermocouples. The large internal volume (from 5 to 10 l) which was a special feature of the apparatus, permitted the excess pressure due to gasification during burning, to be reduced to a minimum. Fig. 1 represents the apparatus made with a longitudinal window and operating at 500 kg/cm².

In this work the burning velocity was determined by the period of luminescence, recorded by a photographic film rotating on a drum at a determined velocity. Hexogene and penthrite were used in the form of tablets of weight 0.4 g, height 7-8 mm and diameter 6.2 mm compressed at a pressure of 2700 kg/cm². The density of the tablets was 94-97% of the specific gravity. The charge was tightly inserted into a glass or quartz cylinder. The ignition was carried out with nichrome wire, thickness 0.2 mm, coiled into a spiral of 3-4 turns.

In a nitrogen atmosphere at normal pressure, hexogene did not ignite as a rule, but in the cases when ignition did occur, the burning did not propagate, but failed. Burning only occurred from 2-3 atm, and up to 200-300 kg per cm² a linear relation was observed—described by equation (1). At pressures of 280-300 kg/cm² and above, the linear relation given by equation (1) did not apply (Fig. 2). At $P = 650-950$ kg/cm² an explosion occurred. From the slope of the straight lines obtained with the co-ordinates $\log U$ - $\log P$, the values of the coefficient B and the power V were determined. Over the range $3 < P < 280-300$ kg/cm², $B = 3.35 \cdot 10^{-2}$ and $V = 0.91$. Over the range $300 < P < 650$ kg/cm², $B = 1.1 \cdot 10^{-17}$ and $V = 7$. From these results the relation between the burning velocity and pressure for the whole range of values of P studies could be expressed by a single equation, the sum of the velocities for the two ranges of pressures

$$U = U_1 + U_2 = 3.35 \cdot 10^{-2} P^{0.91} + 1.1 \cdot 10^{-17} P^7 \quad (2)$$

Hence, the result is derived that the burning of hexogene at constant external pressure occurs by two mechanisms which depend on the pressure in different ways. The first term of the equation characterizes stationary burning

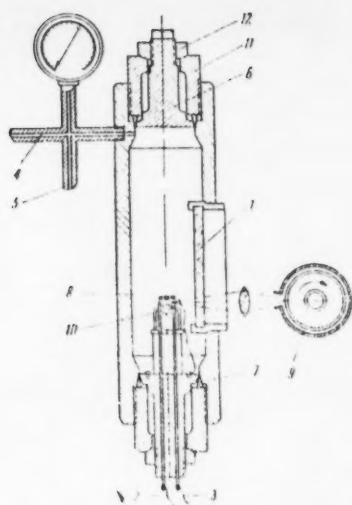


Fig. 1. Constant pressure bomb BD-500. 1) Observations window; 2) and 3) electrical leads; 4) inlet for supply of compressed air; 5) pressure reduction tube; 6) large head; 7) obturator; 8) ignition spiral; 9) photorecorder; 10) high explosive tablet; 11) adjustable screw; 12) sealing nut.

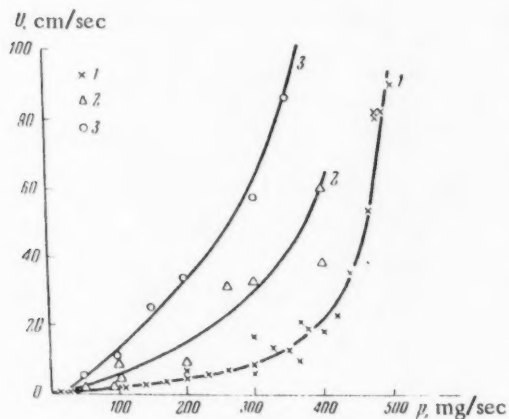


Fig. 3. The relation $U = f(p)$ with different density of the charges. 1) Compressed at 2732 kg/cm²; 2) compressed at 1366.2 kg/cm²; 3) compressed at 545.5 kg/cm².

depending on the external pressure in different ways. The first case is of course realized at low pressures. With an increase of pressure the burning occurs more in the pores and it also proceeds in the gas which is formed by the decomposition of the high explosive on its highly developed surfaces.

Due to the inability of the gases to escape easily a critical pressure develops inside the tablet when the reaction rate abruptly increases and non-stationary burning conditions occur accompanied by explosion or detonation. Hence it also follows with increase of pressure that with a lower charge density there must be an earlier transition

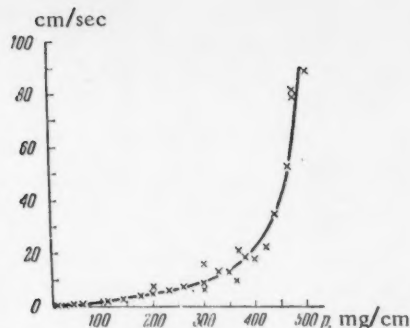


Fig. 2. Relation between burning velocity of hexogene and pressure.

in the range $3 < P < 280 \text{ kg/cm}^2$. Here $U_1 \gg U_2$; the second term corresponding to pressures from 300 to 600 kg/cm² strongly depends on P and describes a non-stationary regime occurring with a velocity of $U_2 \gg U_1$, which passes over to give an explosion at $P > 600 \text{ kg/cm}^2$. With $P = 300 \text{ kg/cm}^2$ $U_1 = U_2$. The equation describing the relation between the burning velocity and pressure for penthrite only differs from the same equation for hexogene in the values of the coefficient B and the power V . Over the whole range of pressures $U = U_1 + U_2 = 1.26 \cdot 10^{-2} P + 1 \cdot 10^{-13} P^{5.5}$. Burning only begins when the pressure $P = 10 \text{ kg/cm}^2$.

The results of our tests are found to be in agreement with the theory of Zeldovich [7]. However, the basic physical concept based on this theory—that the upper layer of the high explosive evaporates—is evidently only applicable at low pressures not exceeding atmospheric. At high pressures, as indicated by Belyaev and Zeldovich, it is difficult to consider burning as a process of evaporation. If it is assumed under our conditions with a pressure of up to several dozen atmospheres that burning continually occurs in the vapour phase, then the sudden transfer from the normal process of burning to non-stationary conditions must take place at relatively low pressures (20-30 kg/cm²) and consequently burning must therefore be transferred into the condensed phase and the velocity must be increased in proportion to the pressure by a power of 2 or 3. In fact, as is clear from the experiments which we have described, this is not observed.

From our investigations it is possible to reach the conclusion that burning evidently occurs in the gas phase, predominantly consisting of products of incomplete chemical decomposition, simultaneously—both over the burning surface and inside the tablet—with different velocities in the pores,

from burning with a small velocity to high velocities and a non-stationary regime. Fig. 3 shows the relation $U = f(p)$ of hexogene for tablets of the charges manufactured at different pressures.

SUMMARY

1. The effect of high pressures on the burning of secondary high explosives has been investigated.
2. An empirical equation for the relation between the burning velocity and pressure over the range from 1-900 cm² has been obtained.
3. Burning in the gas evidently proceeds over the burning surface and in the pores of the charge with different velocities, the difference depending on the external pressure.

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ON THE NATURE OF POROSITY OF CHROMIUM HYDROXIDE GELS

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It is known that after the dehydration of many minerals, crystal hydrates, and hydrated oxides, a porosity develops the nature of which is determined by the conditions of dehydration and the nature of the initial products [1-3]. In a number of cases pores are formed the openings of which are of the same order of magnitude as the dimensions of molecules of substances used to investigate the structure of pores. The nature of pores exerts a significant effect not only on the kinetics of various heterogenic processes, but also on equilibrium adsorption and the energy of the interaction involved in adsorption. For this reason, knowledge of the distribution of pores in porous materials is of considerable interest. In the work described, the adsorption method was used to investigate the porosity of several samples of hydrated chromium oxide as it was affected by the conditions of preparation of the samples and their subsequent treatment.

EXPERIMENTAL

The samples were prepared by precipitation with 10% ammonia from an aqueous solution of chromium nitrate. The conditions of precipitation differed as far as the pH and the temperature at which precipitation was carried out were concerned. Sample 1, which had a grey-green coloration, was precipitated at pH = 8.8 and a temperature of 40°. Samples 2 and 3, which were black, had been precipitated at room temperature at pH = 7.0 and pH = 8.0, respectively. On being washed, the precipitates were molded and dried to constant weight at 120°. Conclusions in regard to the nature of the porosity of the samples of chromium hydroxide gels thus prepared were drawn on the basis of data pertaining to the adsorption of argon and water vapor. Prior to the adsorption experiments the samples were kept in vacuum at room temperature. Thereupon adsorption and desorption of argon at minus 195° and of water vapor at 20° were studied. After this, the samples were heated in vacuum at 350° for several days. In this manner, samples 1-D, 2-D, and 3-D were obtained, on which an investigation of adsorption was carried out in the same order. The adsorption of argon was investigated in the initial range to a relative pressure of $p/p_s = 0.2$, that of water vapor in the whole range to saturation. The table gives values obtained for the adsorption of argon and water vapor on six samples of chromium hydroxide gel at $p/p_s = 0.1$ and also for the adsorption of water vapor at saturation ($p/p_s = 1$).

Values for the Adsorption of Argon and Water Vapor*

Temp. of evac- uation, °C	Argon, mM/g, $p/p_s = 0.1$	Water	
		mM/g, $p/p_s = 0.1$	cm ³ /g, $p/p_s = 1$
20	(1) 0.6	2.5	0.10
20	(2) 0.2	3.7	0.13
20	(3) 3.5	4.3	0.26
350	(1-D) 1.5	2.7	0.09
350	(2-D) 2.2	4.0	0.10
350	(3-D) 3.9	4.5	0.22

*The number of samples are given in parenthesis.

DISCUSSION OF EXPERIMENTAL RESULTS

Comparison of the values for the adsorption of argon with those for the adsorption of water vapor indicates that the chromium hydroxide gels which were prepared had a greater adsorptive capacity for water vapor (from 2.5 to 4.5 mM/g at a relative humidity of 0.1). However, one must note that these values represent reversible adsorption of water vapor, because in the region of small p/p_s ratios the adsorption and desorption isotherms practically coincide, and the adsorbed water can be completely removed in vacuum at 20° within several hours. The maximum quantity of water vapor that was adsorbed at $p/p_s = 1$ by the samples 3 and 3-D, which had the greatest adsorptive capacity (0.26 cm³ per g and 0.22 cm³/g), is equivalent to the corresponding value for active dryers, silica gels with narrow pores having a predominant pore diameter of approximately 25 Å. Samples D and 3-D also adsorbed argon molecules well (3.5 mM/g and 3.9 mM/g at $p/p_s = 0.1$). One

may therefore conclude that the majority of pores of the samples under investigation were also accessible to argon molecules. As distinguished from samples 3 and 3-D, samples 1 and 2 had ultra-small pores, so that the molecules of argon could not penetrate into most of these pores. Consequently, the value for the adsorption of argon at $p/p_s = 0.1$ on sample 2 was more than by one order (by a factor of 17) smaller than that for its adsorption on sample 3, whereas the adsorption values for water vapor on these two samples did not show any significant difference. The small adsorption value for argon found in the case of sample 2 must have been due to adsorption on the outer, rough surface of the chromium hydroxide gel particles. These particles are interpenetrated by channels, the openings of which have a diameter of approximately 3 Å and can be entered only by very small molecules. The outer surface must be equal to approximately 30 m²/g and the inner surface of the channels to approximately 800 m²/g, if one assumes that the molecular area for one molecule of water adsorbed on two hydroxyls has a magnitude of 25 Å², just as in the case of silicas [4]. One may therefore regard sample 2 as belonging to the class of molecular sieves of type A4[5], which are also effective dryers. However, as distinguished from the thermally stable aluminosilicate zeolites, the chromium hydroxide gels were found to undergo structural changes on being heated in vacuum to 350°: the microporosity effect disappeared to a considerable extent, a part of the narrow pores were closed by sintering (the magnitude of the specific surface calculated on the basis of adsorption of water vapor dropped by 10-20%), and another part of the narrow pores were widened until their diameter reached the dimensions of argon and hydrocarbon molecules.

The number of argon molecules adsorbed by sample 1 at $p/p_s = 0.1$ was four times smaller than the quantity of adsorbed water molecules, but only 2.5 times smaller than the number of argon molecules adsorbed by sample 1-D. On the basis of a comparison between the adsorption values for argon and water vapor one may conclude that sample 1, which was precipitated from alkaline solution that had been heated, exhibited a relatively low adsorption capacity for water vapor and a comparatively small microporosity effect, while at the same time showing a sufficiently high stability towards the effects of heat treatment in vacuum. Apparently a higher acidity of the solution contributes to the formation of a greater number of particle nuclei, so that the rate of growth of the particles is not very great. This results in the formation of a chromium oxide hydrogel with a denser structure and with narrow channels forming interstices between the particles.

SUMMARY

1. The adsorption of argon at minus 195° and of water vapor at 20° on six samples of chromium hydroxide gel prepared under different conditions was investigated.
2. By varying the conditions of precipitation, one may prepare hydrated chromium oxides with different types of porosity, including chromium oxides which have a pore structure that is characteristic for molecular sieves of the aluminosilicate type.

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THE COMPOSITION OF MIXTURES OF PRODUCTS
OF THE CHLOROMETHYLATION OF 2-ACETOTHIENONE
IN THE PRESENCE OF AN EXCESS OF ALUMINUM CHLORIDE
AND THE SYNTHESIS OF 4- AND 5-FORMYL AND 4-
AND 5-HYDROXYMETHYL-2-ACETOTHIENONES

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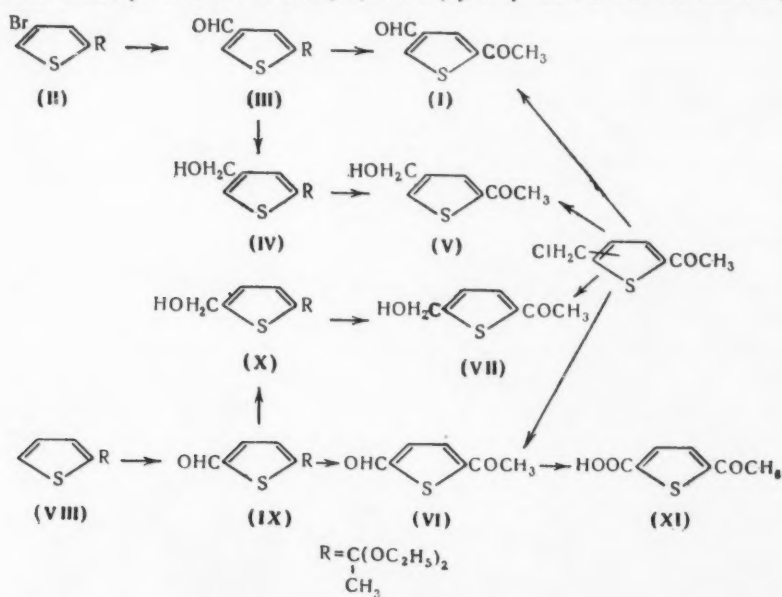
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In an earlier communication dealing with the chloromethylation of acetophenone and 2-acetothienone in the presence of an excess of aluminum chloride [1], it was shown that the first of these two substances forms *m*-(chloromethyl)-acetophenone and the second a mixture of 4- and 5-(chloromethyl)-2-acetothienones. The approximate ratio of the isomers was estimated by us on the basis of the quantities of methylglutaric and adipic acids which formed from the chloromethylacetothienones after the latter had undergone a 4-stage conversion. Because data on the composition of the mixture in question could be used to interpret the characteristics of the chloromethylation process carried out under the conditions described by us, it appeared of interest to establish more precisely the content of each of the isomers. To do this, the mixture of chloromethylacetothienones was converted by a one-stage process into a mixture of ketoaldehydes, and the quantity of individual components in the latter mixture was determined polarographically. To determine the initial constants of the ketoaldehydes, it was necessary to have them in a pure state. For this purpose, a synthesis of the 4- and 5-formyl-2-acetothienones was undertaken. 4-Formyl-2-acetothienone (I) was synthesized from the diethylketal of 4-bromo-2-acetothienone (II) [2, 3]. From the latter, by using a method proposed by Gronovitz [4], the diethylketal of 4-formyl-2-acetothienone (III) was obtained. Hydrolysis of the diethylketal yielded the ketoaldehyde (I). Furthermore, (III) was reduced with NaBH_4 [5] to the diethylketal of 4-(hydroxymethyl)-2-acetothienone (IV), which on hydrolysis gave 4-(hydroxymethyl)-2-acetothienone (V). The preparation of 5-formyl-2-acetothienone (VI) and 5-(hydroxymethyl)-2-acetothienone (VII) was carried



out analogously from the diethylketal of 2-acetothienone (VIII) over the diethylketals of 5-formyl-2-acetothienone (IX) [6] and 5-(hydroxymethyl)-2-acetothienone (X).

Comparison of the physical constants of a benzoate obtained from the mixture of hydroxymethyl compounds derived from the chloromethylation products with those of the benzoates of the isomeric alcohols (VII) and (V) showed that this benzoate is a derivative of a ketoalcohol having the constitution (V). A benzoate corresponding to (VII) could not be isolated from the mixture.

A polarographic analysis of the mixture of formyl derivatives prepared by the Sommelet reaction from the chloromethyl derivatives and of the isomer that were synthesized showed that the mixture which had not been purified and consisted to 85% of aldehydes contained 69% of the 4-isomer and 16% of the 5-isomer, which corresponds to a ratio of 4.3 : 1. Study of UV-spectra demonstrated that the ketoaldehydes isolated by us from the mixture of products of the Sommelet reaction was identical with the 4-isomer (I). An isomer of the structure (VI) could not be isolated from the mixture. The structure of (VI) was confirmed by oxidation to 5-acetylthiophene-2-carboxylic acid (XI). The constants of the acid obtained, as had already been shown on a former occasion of our laboratory [7], do not correspond to those reported for this acid by Hartough and Kosak [8].

EXPERIMENTAL

Diethylketal of 4-bromo-2-acetothienone (II). To 20.5 g of 4-bromo-2-acetothienone [2] in 15 ml, of absolute alcohol 22 g of orthoformic ester and 2 drops of concentrated HCl were added. After 20 hr the mixture was neutralized with an alcoholic solution of sodium ethylate and filtered. On evaporation of the alcohol the residue was distilled in vacuum. At 118-125° (8 mm) 24.7 g of product (II) went over and were collected (yield 88.8%). Repeated distillation of this ketal, as well as of the other ketals described below, resulted in partial splitting off of alcohol, so that the index of refraction was changed. For the same reason, values for C and H that were too high were obtained.

Diethylketal of 4-formyl-acetothienone (III). To 40 ml of an ether solution of butyl lithium containing 2.9 g of C_4H_9Li and brought down to a temperature of minus 70°, a cooled to minus 70° solution of 9.7 g of II in 20 ml of absolute ether was added while a stream of nitrogen was passed through. The solution obtained in this manner was added 5 min later under cooling with ice to 4.4 g of $HCON(CH_3)_2$ in 5 ml of absolute ether. The suspension which was formed agitated for 2 hr. On the following day it was poured on ice and extracted with ether. The ether extract was washed and dried over $CaCl_2$. The yield of III was 5.2 g (66%); b. pt. 128-134° (5 mm).

4-Formyl-2-acetothienone (I). A mixture of 1 g of III, 3 ml of CH_3OH , and 1 ml of concentrated HCl was heated to boiling and poured into water. The substance I which precipitated was filtered off; b.p. 86-86.5 after two recrystallizations from aqueous alcohol, yield 0.7 g. (98%). λ_{max} (in alcohol) 240 m μ (ϵ 29,100). Found: C 54.59; 54.80; H 3.76; 3.95; S 20.62; 20.80%. $C_7H_6O_2S$. Calculated: C 54.53; H 3.92; S 20.79%.

4-Hydroxymethyl-2-acetothienone (V). To 5 g of III in 40 ml of CH_3OH at 8-15° a solution of 0.42 g of $NaBH_4$ in 8 ml of water containing 1 drop of a 40% solution of NaOH was added dropwise during 8 min. The pH of the solution was brought to 6 with glacial CH_3COOH and 5 min later to 3 with H_2SO_4 . Water was added and the mixture extracted with ether; after the ether had been distilled off, the residue (3.5 g) was dissolved in 8 ml of CH_3OH and hydrolyzed similarly to III. The mixture was poured into water and extracted with ether; the ether extracts were dried over $MgSO_4$. After the ether had been distilled off, 1.5 g of an oil (yield 43.5%) remained. This oil decomposed during distillation in vacuum. The benzoate (from alcohol) had a m.p. of 76-76.5°. Found: C 64.02; 64.34; H 4.60; 4.62; S 12.30; 12.39%. $C_{14}H_{12}O_3S$. Calculated %: C 64.60; H 4.65; C 12.32%. The benzoate obtained from the mixture of alcohols derived from the chloromethylation products [1] melted at 76-76.5° and gave no melting point depression when mixed with the benzoate from V. Found: C 64.12; 64.37; H 4.77; 4.44; S 12.23, 12.34%. $C_{14}H_{12}O_3S$. Calculated: C 64.60; H 4.65; S 12.32%.

Diethylketal of 2-acetothienone (VIII). VIII was prepared similarly to II from 25.6 g of 2-acetothienone. Yield 21.6 g (54.1%); b.p. 85-89° (9-11 mm).

Diethylketal of 5-formyl-2-acetothienone (IX). To 38 ml of an ether solution of butyl lithium (2.75 g of C_4H_9Li) 8.6 g of VIII in 40 ml of absolute ether were added within 20 min. The mixture was cooled with ice and salt and nitrogen was passed through it during the reaction. After 30 min the mixture was poured into a solution of 4.7 g of $HCON(CH_3)_2$ dissolved in 30 ml of absolute ether and worked up as described in the case of III. Yield 4.7 g (47.6%); b.p. 129-137° (5 mm).

5-Formyl-2-acetothienone (VI). VI was prepared similarly to I by hydrolyzing the ketal. Yield 74.1%; m.p. 104-105° (from a hexane-benzene mixture); λ_{\max} (in alcohol) 292 m μ ; (ϵ 11,500). Found: C 54.64; 54.83; H 4.01; 3.96; S 20.57; 20.56%. $C_7H_6O_2S$. Calculated: C 54.53; H 3.92; S 20.79%.

5-Hydroxymethyl-2-acetothienone (VII). By reacting 3.5 g of IX with 0.3 g of NaBH₄, VII was prepared similarly to V. Yield 1.6 g (65.8%); m.p. of the benzoate (from alcohol) 92-92.5°. Found: C 64.85; 64.97; H 4.64; 4.81; S 12.26; 12.37%. $C_{14}H_{12}O_3S$. Calculated: C 64.60; H 4.65, S 12.32%.

5-Acetyl-2-thiophenecarboxylic acid (XI). To a suspension of Ag₂O prepared from 1.6 g of AgNO₃ and 0.76 g. of NaOH and containing 7 ml of water 0.7 g of VI were added within 10 min; the mixture was shaken for 30 min. Working up of the mixture yielded XI with a m.p. of 205.5-206° (from water), which did not give a melting point depression in a mixed sample with XI prepared from ethyl-(5-acetyl-2-tenyl) sulfone [7].

Sommelet reaction of mixture of 4- and 5-(chloromethyl)-2-acetothienones. A mixture of hexamethylene-tetramine salts was obtained from 6.9 g of the mixture of chloromethyl derivatives [1] and 5.5 g of hexamethylene-tetramine in 12 ml of CCl₃H; yield 11.5 g (93%). Five grams of the salts, 20 ml of CH₃COOH, and 30 ml of water were boiled for 30 min. The mixture was extracted with ether; the ether extract was neutralized with soda and evaporated. The residue consisted of 0.8 g of a mixture of ketoaldehydes (yield 31%, m.p. 56-74°), which was subjected to spectral and polarographic analysis. λ_{\max} (in alcohol) 240 m μ (ϵ 17,000); 285 m μ (ϵ 6600). After four-fold crystallization from aqueous alcohol, a product was isolated which had a m.p. of 86-87° and did not give a melting point depression in a mixed sample with I. λ_{\max} (in alcohol) 240 m μ (ϵ 26800). Found: C 54.72; 54.62; H 3.97; 3.83; S 20.77; 20.60%. $C_7H_6O_2S$. Calculated: C 54.53; H 3.92; S 20.79%. From the products contained in the mother liquors no substance melting above 86° could be isolated.

SUMMARY

1. Starting from the diethylketals of 2-acetothienone and 4-bromo-2-acetothienone, 5-formyl-2-acetothienone and 4-formyl-2-acetothienone were synthesized.
2. It was established on the basis of data obtained by polarographic analysis that in the mixture of ketoaldehydes obtained from the chloromethyl derivatives of 2-acetothienone, the 4- and 5-isomers were present in a ratio of 4.3 : 1.

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1-ALKOXYCYCLOHEXENES

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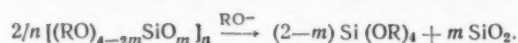
Original article submitted May 9, 1960

1-Alkoxy cyclohexenes, which are representatives of α, β -unsaturated ethers containing a double bond in the hydrocarbon ring, have not been investigated very thoroughly hitherto. The method of their synthesis described in the literature is based on splitting off of alcohol from cyclohexanone ketals by using a mixture of phosphoric acid anhydride with pyridine [1-3] or of benzoyl chloride with quinoline [4], by reacting with p-toluenesulfonic acid [5], or by thermal decomposition [6]. It has also been reported that it is possible to prepare cyclohexen-1-yl alkylethers by reducing alkoxy derivatives of dihydrobenzene with sodium in liquid ammonia [7].

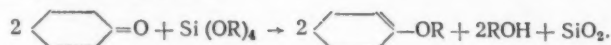
We have developed a novel, simple, convenient, and cheap method for the preparation of 1-alkoxy cyclohexenes. It is based on the reaction of tetraalkoxysilanes with cyclohexanone, which takes place in the presence of a quantity of orthophosphoric acid sufficient to exert a catalytic effect and proceeds according to the following scheme:



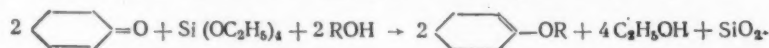
where R = alkyl, $0.5 \leq m \leq 2$, and $n \geq 2$. An intermediate product of this reaction is the corresponding cyclohexanone ketal, which splits off an alcohol during distillation in the presence of traces of H_3PO_4 . The synthesis was carried out by heating to boiling a mixture of cyclohexanone with the appropriate tetraalkoxysilane, which contained the reacting substances in a molar ratio of 1.4-1.5, in the presence of approximately 1 mol.% of 80-100% H_3PO_4 . The alcohol that formed was distilled off slowly and the 1-alkoxy cyclohexene was separated by fractional distillation at reduced or atmospheric pressure in the presence of metallic sodium (to eliminate traces of alcohol and cyclohexanone). After distillation a mixture of polysilicic esters of different condensation degrees remained. This mixture can be, if necessary, depolymerized by distillation in the presence of 5-10 mol.% of KOH [8]:



In this case the use of tetraalkoxysilane in the conversion will be lowered considerably and the reaction will proceed according to the following general equation:

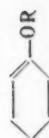


To prepare the higher 1-alkoxy cyclohexenes (beginning with R = $\text{c-C}_3\text{H}_7$), one can to advantage dispense with the application of tetraalkoxysilanes, replacing them with a mixture of tetraethoxysilane (or tetramethoxysilane) and the appropriate higher alcohol. The reaction then takes place according to the equation:



By applying the methods described, we synthesized with yields amounting to 55-70% of the theoretical five 1-alkoxy cyclohexenes, the physical properties of which are listed in the table. Cyclohexen-1-yl-alkyl ethers are colorless liquids with a pleasant odor, which are stable to the action of water and aqueous alkalis, but are readily hydrolyzed by dilute acids into cyclohexanone and the corresponding alcohol. As far as their properties are concerned, they resemble vinylalkyl ethers in that they easily add halogen, hydrogen, and other reactive substances, are oxidized to adipic acid by a solution of permanganate in acetone, and are converted to epoxy compounds by percarboxylic acids. However, they do not polymerize as readily as vinyl-alkyl ethers.

1-Alkoxy-cyclohexenes



R	B. pt. °C (p mm Hg)	d_4^{20}	n_D^{20}	MR		Found, %		Calc., %		Yield, %
				found	calc.	C	H	C	H	
CH ₃	145.0 (760)	0.9224	1.4613	33.39	33.50	75.07	10.94	74.95	10.78	70.9
C ₂ H ₅	63.5 (24)	0.9150	1.4589	37.70	38.12	76.55	11.21	76.14	11.18	63.2
C ₃ H ₇	67 (9)	0.8901	1.4580	42.99	42.74	77.17	11.49	77.09	11.50	60.0
p-C ₄ H ₉	83 (10)	0.8912	1.4602	47.42	47.36	77.95	11.82	77.87	11.76	60.2
i-C ₄ H ₉	90 (9)	0.885	1.4599	52.0	51.97	78.45	11.93	78.51	11.98	55.0

EXPERIMENTAL

Initial reacting substances. The cyclohexanone was dried for 48 hr. by being kept over anhydrous sodium sulfate, after which it was distilled (b.p. 155-156°, n_D^{20} 1.4509) [9]. The synthesis of the initial tetraalkoxysilates and their physical properties have been described before [10]. The n-propyl and n-butyl alcohols were distilled in the presence of metallic calcium; they had physical constants which corresponded to those reported in the literature [9]. As a catalyst 85% H₃PO₄ (analytical reagent grade) was applied, which had a syrupy consistency.

1-Methoxycyclohexene. A mixture of 68.7 g (0.7 M) of cyclohexanone, with 76.1 g (0.5 M) of tetramethoxysilane and 1 g of H₃PO₄ was boiled under reflux for 12 hr. By distilling the reaction mixture from the flask in which the reaction had been carried out, 20.5 g (91%) of methyl alcohol with a b.p. of 64-65° and 65 g of crude 1-methoxycyclohexene with a b.p. of 130-140° were obtained; a second distillation of the latter in the presence of metallic sodium yielded 55.7 g of pure substance with a b.p. of 143-145°, i.e., 71% of theory. After fractionation with the use of a column, the 1-methoxycyclohexene had the physical constants which are listed in the table.

1-Ethoxycyclohexene. A mixture of 68.7 g (0.7 M) of cyclohexanone, 104.2 g (0.5 M) of tetraethoxysilane, and 1 g of H₃PO₄ was boiled under reflux for 12 hr and then slowly distilled. First 32.2 g (100%) of ethanol with a b.p. of 78-80° were separated. The fraction which went over after this and had a b.p. of 140-160° was shaken for 30 min with 200 ml of 30% NaOH, washed with water, dried over potassium carbonate, and then distilled twice, first at atmospheric pressure and then in vacuum in the presence of metallic sodium. The yield of 1-ethoxycyclohexene with b.p. = 62-64° (24 mm) was 55.8 g, i.e., 63.2% of theory.

1-Butoxycyclohexene. A mixture consisting of 68.7 g (0.7 M) of cyclohexanone, 104.2 g (0.5 M) of tetraethoxysilane, 222.3 g (3 M) of n-butyl alcohol, and 1 g of H₃PO₄ was boiled under reflux for 12 hr and then distilled. At 78-80° 81.8 g (88%) of ethyl alcohol went over, at 80-116°, 59 g of butyl alcohol containing some ethyl alcohol, and at 116-118°, 76 g of n-butanol. After this repeated fractional distillation of the residue yielded 65.0 g (60.2%) of 1-butoxycyclohexene with a b.p. of 202-204°, which after repeated distillation in vacuum in the presence of metallic sodium had the physical constants listed in the table. When the distillation residue from the reaction mixture was slowly distilled in vacuum in the presence of 2 g of powdered NaOH, 44.8 g (14 M) of tetrabutoxysilane with a b.p. of 154-160° (14 mm), n_D^{20} 1.4150, were obtained in addition to the products mentioned above. The tetrabutoxysilane could be used for subsequent syntheses. 1-Propoxycyclohexene was prepared similarly to 1-butoxycyclohexene.

1-Isoamyloxycyclohexene. A mixture of 59.0 g (0.6 M) of cyclohexanone with 150.6 g (0.4 M) of the tetraisoamyloxysilane and 1 g of H₃PO₄ was heated to boiling for 14 hr. Subsequent slow distillation of the reaction mixture resulted in the separation of 48.3 g (91%) of isoamyl alcohol with a b.p. 128-132°. Fractional vacuum distillation of the residue yielded 55.6 g (55%) of 1-isoamyloxycyclohexene with a b.p. of 95-98° (10 mm).

SUMMARY

1. A method has been developed for the synthesis of 1-alkoxycyclohexenes which is based on a reaction between cyclohexanone and tetraalkoxysilanes that is catalyzed by H_3PO_4 .
2. Five compounds of this type have been synthesized and described.

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CHARACTERISTICS OF THE MELTING OF GLAUBER SALT AT HIGH PRESSURES

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Knowledge of the influence which pressure exerts on the conditions under which Glauber salt melts is of importance from the standpoint of determination of the ranges of stability of this salt as well as of ternadite in the earth's crust. Tamman [1, 2] and a number of other investigators [3-5] studied the effect of pressure on the temperature of melting of Glauber salt (Fig. 1). The assumption was made that the incongruent character of melting, which is typical for this salt at atmospheric pressure, is preserved at high pressures. Only Geller [4] admitted the possibility that the character of melting may change, having found that the melting temperature curve exhibits the break A-B at high pressures (Fig. 1). However, his experiments were carried out under special conditions (the pressure was transmitted through clay) which, in Tamman's opinion [2], was the reason for the anomalous shape of the resulting curve.

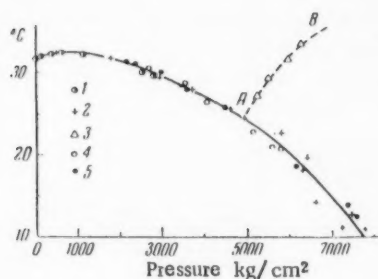


Fig. 1. Dependence of the temperature of melting of Glauber salt on the pressure. Data by 1) Tamman [1]; 2) Tamman and Wibel [2]; 3) Geller [4]; 4) Adams and Gibson [5]; Kryukov and Manikhin.

We also investigated initially the dependence of the temperature of melting on the pressure in the range up to 8000 kg/cm². The salt was subjected to pressure in an apparatus usually employed by us for pressing solutions out of rocks [6]. To keep the temperature constant, the apparatus was placed in a container through which water coming from a TS-15 temperature regulating device was circulated. The apparatus together with the container installed between the plates of a 60-ton hydraulic press. After the desired temperature had been established, the pressure, which was controlled by means of a standard gauge, was raised until fusion of the salt set in, whereupon a part of the melt was ejected through a release opening with which the apparatus was provided and the pressure of the working liquid in the press dropped sharply. The data obtained by us are plotted in Fig. 1 (black circles). Although these data fit into the curve constructed on the basis of data reported by Tamman and other investigators (with the exception of the branch of the curve based on Geller's results), we did not regard this as a proof that the incongruent character of melting is preserved in the whole range of pressures which had been applied by us. To obtain an answer to the question involved, we considered it necessary to conduct direct experiments and analyzed for this purpose melts which were obtained from the Glauber salt at high pressures. Melting of the salt and taking of samples of the liquid phase was carried out by means of the apparatus shown in Fig. 2. The principal parts of this apparatus are a high-pressure cylinder, an outlet vent with a ball valve, and a chamber serving as a receptacle for samples. Regulation of the temperature in the apparatus was accomplished as described above. For every experiment the pressure and temperature were preset on the basis of the relationship between them which had been established previously (Fig. 1). The temperature was made to exceed by 0.1-0.2° that corresponding to equilibrium and was kept constant for 1 hr, to make sure that in the case of incongruent melting any anhydrous sodium sulfate which

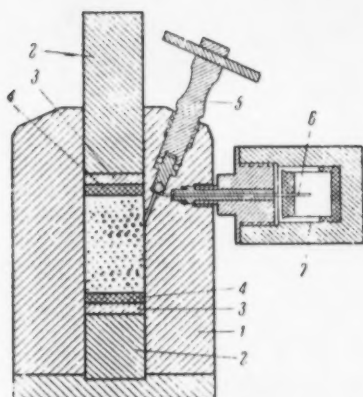


Fig. 2. Apparatus for investigation of the melting of crystal hydrates at high pressures. 1) Cylinder (2Kh-13 steel); 2) pistons (ShKh-15); 3) ebonite lining; 4) rubber lining; 5) valve; 6) needle; 7) receptacle.

ceeded the content of water in Glauber salt (55.9%), which was in accordance with the assumption that the melting was of an incongruent type in the range in question. However, as the pressure was increased, the composition of the melt approached more and more closely that of Glauber salt, becoming identical with that of Glauber salt at pressures greater than 5000 kg/cm². This was apparently due to the fact that the solubility of anhydrous sodium sulfate increased with increasing pressure, so that its concentration in the solution finally reached a limiting ratio corresponding to the decahydrate.

SUMMARY

1. An apparatus has been designed which makes it possible to investigate the characteristics of melting of crystal hydrates at high pressures.

2. It was established that at pressures exceeding 5000 kg/cm² the melting of Glauber salt takes place congruently because of the increase in the solubility of anhydrous sodium sulfate as the pressure is increased.

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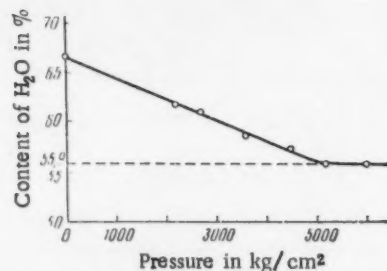


Fig. 3. Water content of the melt in relation to the pressure.

formed, would have time to precipitate. After this the high-pressure valve was opened, so that a sample of the solution from the upper part of the chamber was ejected through the needle into the glass receptacle, where the melt crystallized immediately if the pressure which had been established was high enough. The content of water in the sample was determined by drying at 110°.

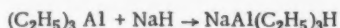
The results obtained indicated (cf. Fig. 3) that the water content of the melt at pressures lower than 5000 kg/cm² ex-

REDUCTION OF ALKYLCHLOROSILANES WITH SODIUM HYDRIDE IN THE PRESENCE OF TRIETHYLALUMINUM

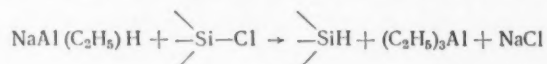
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To reduce alkyl or aryl chlorosilanes, lithium aluminum hydride is used extensively in the laboratory. In a number of investigations [1-3] attempts have been made to use the cheap sodium hydride for reducing Si-Cl to Si-H. However, these attempts have not led to positive results. It has been found recently [4] that alkylchlorosilanes can be successfully reduced with sodium hydride if the alkylchlorosilane vapors are passed through a suspension of finely dispersed sodium hydride at 250°. At a lower temperature, for instance 200°, the reaction did not proceed well. We found in the work described in this instance that if a small quantity of triethylaluminum is added to a suspension of sodium hydride in an aromatic hydrocarbon (benzene, toluene, xylene, etc.), the reduction of chlorosilanes takes place readily at 60-80°. The part played by triethylaluminum in this reaction is as follows. Because of its low reactivity towards chlorosilanes at the temperatures involved, triethylaluminum reacts preferentially with the sodium hydride under formation of the complex $\text{NaAl}(\text{C}_2\text{H}_5)_3$, which is soluble in the hydrocarbon:



This complex functions as a reducing agent and converts Si-Cl into Si-H according to the following equation:



The triethylaluminum which is freed according to this equation reacts with a fresh portion of sodium hydride, bringing it into solution in the form of the complex, and so forth. The reduction is carried out in such a manner that the complex $\text{NaAl}(\text{C}_2\text{H}_5)_3$ is always present in the reaction mixture. By applying this method, we reduced trimethylchlorosilane, dimethylchlorosilane, diethyldichlorosilane, methyltrichlorosilane, methylbutyldichlorosilane, phenyltrichlorosilane, phenylmethyldichlorosilane, and γ -phenylpropyltrichlorosilane.

EXPERIMENTAL

Reduction of trimethylchlorosilane. To a suspension of 12 g of finely disintegrated sodium hydride in 60 ml of toluene, 5 ml of triethylaluminum were added; the mixture was kept under agitation at 80° for 10 min. At this temperature 42 g of trimethylchlorosilane were added gradually. The trimethylsilane which formed as a result of the reduction was collected in a cooled receiving vessel. On distillation 24.4 g (89% of theory) of trimethylsilane with a b.p. of 6-7° were obtained.

Reduction of dimethyldichlorosilane. To a suspension of 10 g of sodium hydride in 60 ml of toluene 6 ml of triethylaluminum were added. Reduction of 20 g of dimethyldichlorosilane was carried out as described above. In this manner, 7.8 g (84% of theory) of dimethylsilane with a b.p. of minus 20 - 18° were prepared.

Reduction of diethyldichlorosilane. To a suspension of 18 g of sodium hydride in 60 ml of toluene containing 5 ml of triethylaluminum, 40 g of diethyldichlorosilane were added at 85-90°. The diethylsilane which formed by reduction was distilled off from the reaction mixture. On distillation, 20.4 g (92% of theory) of diethylsilane with b.p. = 56-57°, n_D^{20} 1.3924, were obtained.

Reduction of methyl-n-butyldichlorosilane. To 15 g of sodium hydride in 60 ml of xylene and 6 ml of triethylaluminum, 38 g of methylbutyldichlorosilane were gradually added at 85-90°. After completion of the reduction the product was distilled out of the reaction flask together with a small quantity of xylene. On distillation with the use of a column 18.6 g (82% of theory) of methyl-n-butylsilane with a b.p. of 81-82° were obtained; n_D^{20} 1.3996; d_4^{20} 0.6992. Found: C 58.91; 58.94; H 13.75; 13.70; Si 27.40; 27.28%. $C_5H_{14}Si$. Calculated: C 58.76; H 13.61; Si 27.42%.

Reduction of methyltrichlorosilane. To 22 g of sodium hydride in 90 ml of toluene and 6 ml of triethylaluminum 25 g of methyltrichlorosilane were gradually added at 80-85°. The methylsilane that formed as a result of the reduction was collected in a cooled trap. The yield was 5.4 g (72% of theory) of methylsilane.

Reduction of phenylmethyldichlorosilane. To 9 g of sodium hydride in 50 ml of benzene and 5 ml of triethylaluminum 27 g of phenylmethyldichlorosilane were gradually added at 70-75°. After completion of the reduction all volatile products that had formed were distilled out of the reaction mixture, first at atmospheric pressure and finally in vacuum. On fractionation with the use of a column 12.2 g of phenylmethylsilane (71% of the theoretical yield) were obtained; b.p. 46-47° (20 mm), 139.5-140° (760 mm); n_D^{20} 1.5058; d_4^{20} 0.8895. Found: C 68.61; 68.64; H 8.24; 8.30; Si 23.21; 23.23%. $C_7H_{10}Si$. Calculated %: C 68.79; H 8.19; Si 23.01%.

Reduction of methyltrichlorosilane. To 8 g of sodium hydride in 40 ml of benzene and 5 ml of triethylaluminum 15.5 g of phenyltrichlorosilane were added at 70-75°. After cooling the reaction mixture was carefully poured into acidified ice water. The benzene solution was washed with water and dried over calcium chloride. On fractionation with the use of a column 5.8 g (74% of theory) of phenylsilane with a b.p. of 60-62° (100 mm) were obtained; n_D^{20} 1.5111; d_4^{20} 0.8817.

Reduction of γ -phenylpropyltrichlorosilane. To 18 g of sodium hydride in 55 ml of toluene and 6 ml of triethylaluminum 47.5 g of γ -phenylpropyltrichlorosilane were gradually added at 85-90°. After this all volatile products were distilled off in vacuum from the reaction mixture. On fractionation in vacuum 23 g (82% of theory) of γ -phenylpropylsilane with a b.p. of 76.5-77° (8 mm) were obtained; n_D^{20} 1.5051; d_4^{20} 0.8790. Found: C 72.09; 72.04; H 9.44; 9.48%. $C_9H_{14}Si$. Calculated: C 71.94; H 9.32%.

SUMMARY

It was found that alkylchlorosilanes and arylchlorosilanes can be reduced easily with sodium hydride in a hydrocarbon solution if a small quantity of triethylaluminum is present.

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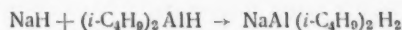
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USE OF SODIUM DIISOBUTYLALUMINUM DIHYDRIDE AS A REDUCING AGENT

L. I. Zakharkin and V. V. Gavrilenko

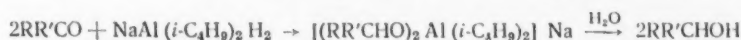
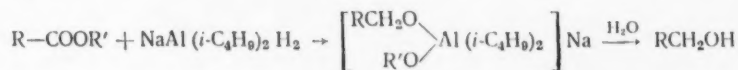
Institute of Organoelemental Compounds, Academy of Sciences, USSR
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In the present communication we are reporting, on the basis of experiments carried out with $\text{NaAl}(\text{i-C}_4\text{H}_9)_2\text{H}_2$, the results of an investigation indicating that it is possible to use addition compounds of dialkylaluminum hydrides with sodium hydride (NaAlR_2H_2) as agents for the reduction of different functional groups in organic substances. The addition compounds or complexes in question exhibit a considerable solubility in a number of organic solvents and have a greater reducing capacity per mole (reduction equivalent) than the corresponding dialkylaluminum hydrides. Sodium diisobutylaluminum dihydride could be easily prepared by interacting sodium hydride with diisobutylaluminum hydride in a benzene or toluene solution at 80-100°:

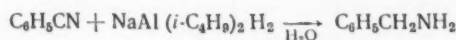
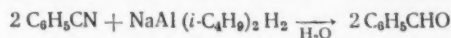


The complex that formed in this reaction was a crystalline compound which dissolved with facility in ether, tetrahydrofuran, benzene, and toluene and was slightly soluble in petroleum ether. It oxidized readily in the air. The solubility of $\text{NaAl}(\text{i-C}_4\text{H}_9)_2\text{H}_2$ in solvents other than ether makes it possible to apply this substance as a reducing agent in cases when the use of ether is undesirable or impossible.

We have reduced methyl benzoate, the methyl ester of δ -chlorovaleric acid, benzaldehyde, cinnamic aldehyde, acetophenone, phenylacetone, and cyclohexanone to the corresponding alcohols according to the following equations:



The yields of the alcohols amounted to 80-95% of theory. Benzonitrile could be reduced either to the aldehyde or to the amine, depending on the conditions under which the reduction was carried out:



By reduction of caproic acid dimethylamide with the dihydride in a benzene solution, dimethyloctylamine was prepared with a high yield.

EXPERIMENTAL

The preparation of sodium diisobutylaluminum dihydride and reduction of the functional groups of organic substances with this reagent were carried out in an inert atmosphere (nitrogen) in an apparatus consisting of four-necked flask equipped with an agitator, a reflux condenser, a dropping funnel, and a thermometer.

Preparation of sodium diisobutylaluminum dihydride. To 13.6 g of sodium hydride suspended in 180 ml of benzene or toluene, 63.0 g of diisobutylaluminum hydride were added in a nitrogen atmosphere. The reaction mixture was heated under stirring to 80-100° during 2-3 hr. To the thick, gel-like mass which formed 100 ml of ether were added after cooling and the turbid solution was allowed to stand overnight. The solution which had cleared was carefully decanted from the unreacted NaH—then the solvent was evaporated in vacuum. The precipitated dihydride

was suspended in hexane, filtered off, and dried in vacuum. In this manner 65 g (88% of theory) of sodium diisobutylaluminum dihydride were prepared the properties of which proved to be identical with those of the same substance described earlier [1]. The sodium diisobutylaluminum hydride was easily soluble in ether and tetrahydrofuran, less easily soluble in benzene and toluene, and soluble with difficulty in hexane.

Reduction of methyl benzoate. To 8 g of the dihydride in 40 ml of ether 5.8 g of methyl benzoate were added under agitation while the ether was kept at the boiling point by the heat of the reaction. The reaction mixture was heated for an additional hour and poured carefully onto ice and with sulfuric acid. The product of the decomposition was extracted with ether and dried over Na_2SO_4 . After evaporation of the ether 4.1 g of benzyl alcohol with a b.p. of 92-93° (10 mm) were obtained; n_D^{20} 1.5406; d_4^{20} 1.0444.

Reduction of the methyl ester of δ -chlorovaleric acid. By reacting similarly 6 g of the methyl ester of δ -chlorovaleric acid with 7.6 g of the dihydride in 40 ml of ether, 4.2 g (87% of theory) of δ -chloroamyl alcohol with a b.p. of 101° (18 mm) were prepared; n_D^{20} 1.4548; d_4^{20} 1.0436; found MR 31.86; calculated MR 31.68. The phenylurethane had a m.p. of 58° (from hexane). Found: C 60.00; 60.30; H 6.52, 6.68%. $\text{C}_{12}\text{H}_{16}\text{NO}_2\text{Cl}$. Calculated: C 59.62; H 6.67%.

Reduction of benzaldehyde. From 10 g of benzaldehyde and 8.6 g of the dihydride in 40 ml of ether 9.2 g of benzyl alcohol were obtained; yield 90% of theory.

Reduction of cinnamic aldehyde. Similarly, from 6 g of cinnamic aldehyde in 10 ml of ether and 4.3 g of the dihydride in 30 ml of ether 5 g of cinnamyl alcohol were obtained. Yield 82% of theory, m.p. 32°.

Reduction of acetophenone. By reacting 6.8 g of acetophenone in 10 ml of ether with 6 g of the dihydride in 30 ml of ether 5.6 g (81% of theory) of α -phenylethyl alcohol with a b.p. of 83-84° (8 mm) were prepared; n_D^{20} 1.5270; d_4^{20} 0.9989. Published data [2] for α -phenylethyl alcohol: b.p. 90° (15 mm); n_D^{15} 1.526; d_4^{15} 1.008.

Reduction of phenylacetone. Reduction of 10 g of phenylacetone in 10 ml of ether with 7.6 g of the dihydride in 40 ml of ether yielded 9 g (90% of theory) of 1-phenylpropan-2-ol with a b.p. of 103° (12 mm); n_D^{20} 1.5226; d_4^{20} 0.9981. Published data [3] for 1-phenylpropan-2-ol: b.p. 101-102° (11 mm); $n_D^{14.5}$ 1.5243; $d_4^{14.5}$ 0.9988.

Reduction of cyclohexanone. Reduction of 5.5 g of cyclohexanone in 10 ml of ether with 5.4 g of the dihydride in 27 ml of ether yielded 4.6 g (82% of theory) of cyclohexanol, b.p. 63-64° (13 mm); n_D^{23} 1.4636; d_4^{20} 0.9618.

Reduction of benzonitrile to the amine. A solution of 3.7 g of benzonitrile in 10 ml of ether was added to a solution of 7.5 g of the dihydride in 75 ml of ether. The contents of the flask were heated for 4 hr under boiling of the ether. The reaction product was decomposed with 10% H_2SO_4 . The acidic aqueous solution was washed with ether and treated with NaOH until the aluminum hydroxide dissolved. The amine which separated was extracted with ether and dried over potassium carbonate. Yield after evaporation of the ether 3.1 g (81% of theory) of benzylamine with b.p. 96° (14 mm); n_D^{20} 1.5448; d_4^{20} 0.9831. Published data for benzylamine [4]: b.p. 90° (12 mm); $n_D^{19.5}$ 1.54406; $d_4^{19.5}$ 0.9827.

Reduction of benzonitrile to the aldehyde. To 5 g of benzonitrile in 10 ml of ether 4.4 g of the dihydride in 30 ml of ether were added. The mixture was heated for 1 hr at the boiling point of ether. On being worked up in the usual manner, the mixture yielded 4.1 g of benzaldehyde (80% of theory), b. p. 75-76° (18 mm); n_D^{20} 1.5445; d_4^{20} 1.0526; m.p. of the 2,4-dinitrophenylhydrazone 237°.

Reduction of the dimethyl of caproic acid. To 3 g of the dimethylamide of caproic acid in 10 ml of benzene 3.3 g of the dihydride in 30 ml of benzene were added. The temperature, which because of the heat evolved in the reaction went up to 70°, was kept at the level corresponding to the boiling point of the benzene for an additional hour. The reaction mixture was decomposed with 10% H_2SO_4 . The acidic aqueous solution was treated with NaOH and the amine which separated was extracted with ether. On evaporation of the ether 2.3 g of dimethyloctylamine were obtained. Yield 83.5% of theory, b.p. 75-76° (10 mm); n_D^{20} 1.4264; d_4^{20} 0.7688; found MR 52.46; calculated MR 52.32; picrate, m.p. 64°.

Published data [5]: dimethyloctylamine picrate, m.p. 62-65°.

SUMMARY

It has been found that sodium diisobutylaluminum dihydride can be applied for the reduction of different functional groups of organic compounds. Both hydrogen equivalents of the complex are utilized.

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SYNTHESIS OF B-TRIALKYLBORAZOLES FROM ESTERS OF ALKYLTHIOBORIC ACIDS

B. M. Mikhailov and T. K. Kozminskaya

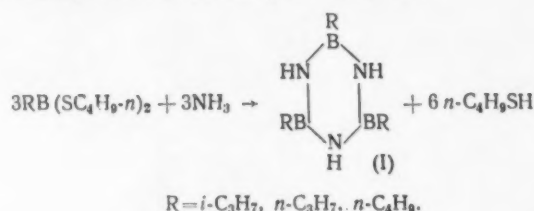
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

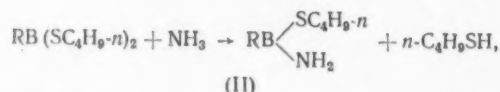
No. 12, pp. 2247-2248, December, 1960

Original article submitted May 16, 1960

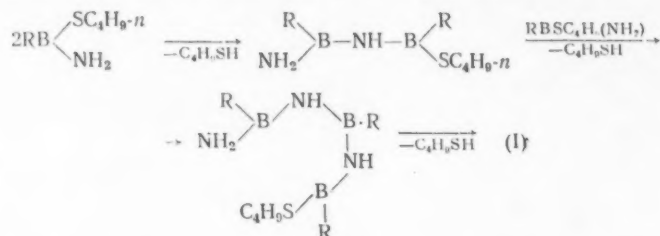
We established recently that the action of ammonia on the di-*n*-butyl ester of isoamylthioboric acid results in the formation of B-triisoamylborazole with a high yield [1]. Further investigation showed that *n*-butyl esters of other alkylthioboric acids also enter into reaction with ammonia. The reaction takes place at room temperature and leads to the formation of B-trialkylborazoles (I) with yields of 80-86%.



The mechanism of the reaction comprises formation in the first stage of an aminothioester (II)



which then apparently condenses into a borazole according to the following scheme:



The initial di-*n*-butyl esters of *n*-propyl and *n*-butylthioboric acids were synthesized by reacting *n*-butyl thiol with the corresponding alkylboron dibromides [1]. The di-*n*-butyl ester of isopropylthioboric acid was also prepared by us for the first time by reacting *n*-butyl thiol with isopropylboron dibromide, which had been synthesized from isopropylboric acid anhydride and boron tribromide by a method described earlier [2]. The B-trialkyl borazole derivatives B-trimethylborazole [3] and B-triethylborazole [1] had been prepared earlier by heating the corresponding boron trialkyls with ammonia in an autoclave at 330-450°.

EXPERIMENTAL

All operations with organoboron compounds were carried out in an atmospheric of dry nitrogen.

Isopropylboron dibromide. By applying the method described earlier [2], 16 g of isopropylboric acid anhydride were reacted with 38.2 g of boron tribromide to prepare 28.5 g (58.3%) of isopropylboron dibromide with a b.p. of 109-113°. After repeated distillation the substance had b.p. 112-113°, d_4^{20} 0.624; n_D^{20} 1.4676. Found: B 5.05; 4.99; Br 73.71; 73.63%. $\text{C}_3\text{H}_7\text{BBr}_2$. Calculated: B 5.07; Br 74.78%.

Di-n-butyl ester of isopropylthioboric acid. After 21.8 g of isopropylboron dibromide had been boiled under reflux with 23.4 g of n-butyl thiol for 12 hr, 18.42 g (78%) of the di-n-butyl ester of isopropylthioboric acid were obtained. B.p. 128.5-129° (7 mm); d_4^{20} 0.9079; n_D^{20} 1.4940.

Found: C 56.99; 57.03; H 10.58; 10.73%. $C_{11}H_{25}BS_2$. Calculated: C 56.83; H 10.85%.

B-Triisopropylborazole. A stream of dry ammonia was passed at room temperature for 40 min, through 17 g of the di-n-butyl ester of isopropylthioboric acid. Slight heating of the reaction mixture took place. After the n-butyl thiol (11.65 g) had been distilled off in vacuum, distillation of the residue in vacuum yielded 4.12 g (82.4%) of B-triisopropylborazole with b.p. 87.5-88° (7 mm); d_4^{20} 0.8453; n_D^{20} 1.4478. Found: C 52.42; 52.49; H 11.55; 11.75; B 15.61; 15.54. $C_9H_{24}B_3N_3$. Calculated: C 52.27; H 11.70; B 15.70%.

B-Tri-n-propylborazole. By reacting similarly 14.5 g of the di-n-butyl ester of n-propylthioboric acid, 3.7 g (86%) of tri-n-propylborazole with b.p. 106.5° (6 mm) were prepared; d_4^{20} 0.8493; n_D^{20} 1.4500. Found: C 52.41; 52.34; H 11.74; 11.84; B 15.59; 15.20%. $C_9H_{24}B_3N_3$. Calculated: C 52.27; H 11.70; B 15.70%. 9.5 g of n-butyl thiol were separated from the reaction mixture.

B-Tri-n-butylborazole. Passing of dry ammonia for 40 min through 14.8 g of the di-n-butyl ester of n-butylthioboric acid resulted in a yield of 8.3 g of n-butyl thiol and of 4.0 g (80.3%) of B-tri-n-butylborazole with b.p. 135.5° (4 mm); d_4^{20} 0.8506; n_D^{20} 1.4540. Found: C 57.89; 57.80; H 11.91; 11.93; B 13.35; 13.14%. $C_{12}H_{30}B_3N_3$. Calculated: C 57.91; H 12.14; B 13.05%.

SUMMARY

It has been found that B-trialkylborazoles are formed smoothly by the reaction of ammonia with alkylthioboric acid esters.

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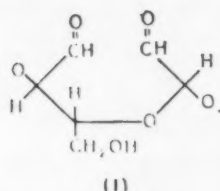
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INVESTIGATION OF DIALDEHYDOCELLULOSES BY MEANS OF INFRARED SPECTRA

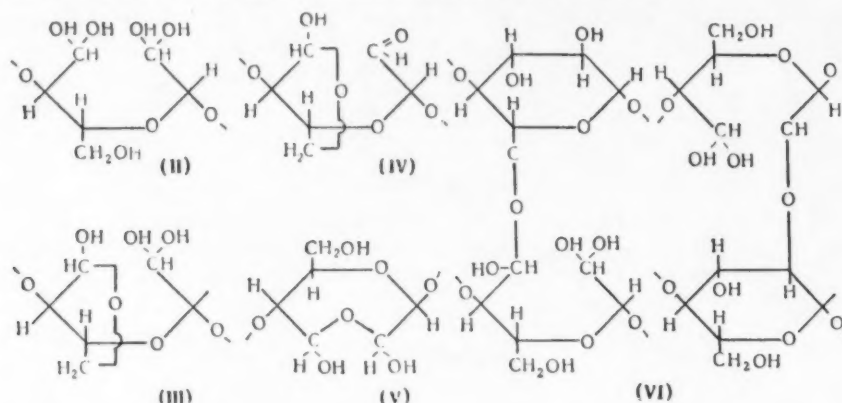
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
No. 12, pp. 2249-2252, December, 1960
Original article submitted May 19, 1960

The action of sodium periodate on cellulose yields dialdehydocellulose [1], which includes the structure (I).



It was shown [2] that the absorption spectra of dialdehydocelluloses do not contain a band in the region of 5.8μ , which is characteristic of the $C=O$ bond, and hence it follows that there are no free aldehyde groups in the structure (I). In this connection it has been suggested in the literature [2-6] that the aldehyde groups in the polyaldehydes are in a bound state in the form of structures (II), (III), (IV), (V), and (VI).



An examination of structures (III), (IV), and (VI) shows that the aldehyde groups in them are in different states. This is confirmed by the different rates of oxidation of the aldehyde groups in positions 2 and 3 by sodium chlorite [7] and also by their capacity to react with only one mole of phenylhydrazine [8]. In the spectra of the dialdehydocelluloses studied we observed absorption in the region of 11μ (910 cm^{-1}) [9]. The intensity of this absorption increased during oxidation of cellulose with sodium periodate under conditions yielding dialdehydocelluloses and decreased as these groups were oxidized with sodium chlorite. Corresponding to this effect, a $C=O$ band at 5.8μ (1740 cm^{-1}), which belonged to the carboxyl groups formed, appeared and increased in intensity.

As we showed in the same work, the absorption in the region of 11μ did not belong to carboxyl groups; in this region, the spectra of dicarboxylcelluloses contained absorption bands of much lower intensity than the spectra of dialdehydocelluloses, while monocarboxycellulose did not absorb at all in the region examined. These data indicate that the absorption band at 11μ belongs to bound aldehyde groups and its intensity increases with the

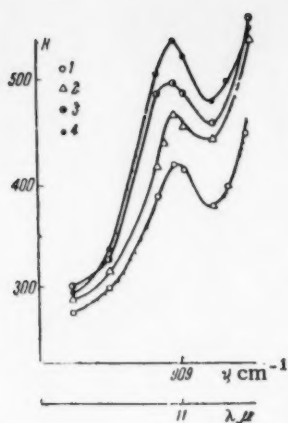
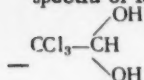


Fig. 1. Absorption spectra of dialdehydocelluloses. Content of aldehyde groups: 1) 0.123; 2) 0.180; 3) 0.230; 4) 0.406 g-equiv. per 100 g of sample.

accumulation of aldehyde groups during the oxidation of cellulose with sodium periodate. The absence of the band at 11μ from the absorption spectra of low-molecular model compounds, such as chloral hydrate



, indicated that the absorption of dialdehydocellulose in

this region does not belong to completely hydrated aldehydes [9, 10], but may be caused by symmetrical valence vibrations of the hemiacetal bond and therefore we consider scheme (III) most probable. It should be noted that absorption in the region of 11μ is associated with mechanical changes [11, 12], but in the present work we show that the bands examined in the spectra of dialdehydocelluloses are connected with definite functional groups and their chemical change.

EXPERIMENTAL

The investigations were carried out on preparations of dialdehydicarboxy-, and tricarboxycelluloses of different degrees of oxidation [13-15] on an IKS-11 spectrophotometer by the method we proposed in [16]. Figure 1 gives absorption spectra of dialdehydocelluloses of different degrees of oxidation. This figure shows that the intensity of

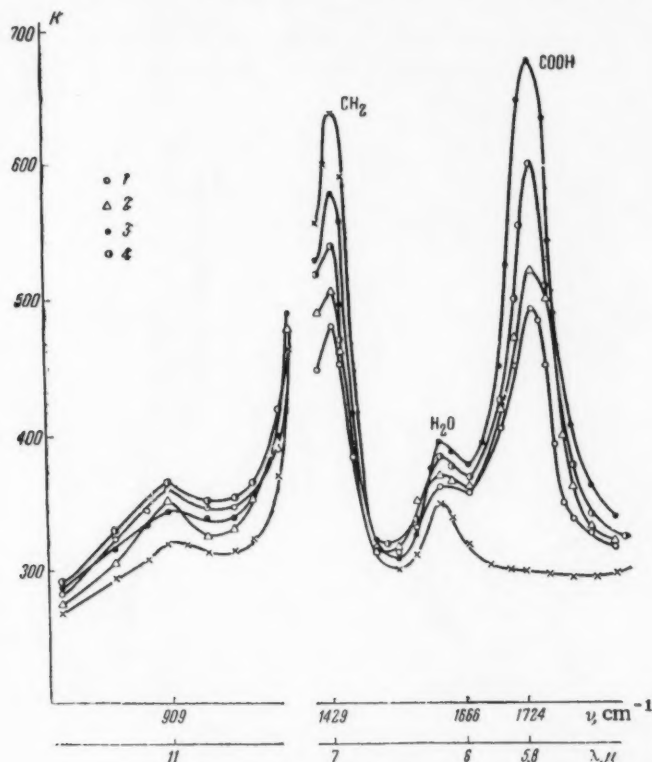


Fig. 2. Absorption spectra of dicarboxycelluloses. Content of carboxyl groups: 1) 0.120; 2) 0.140; 3) 0.225; 4) 0.330 g-equiv. per 100 g of sample.

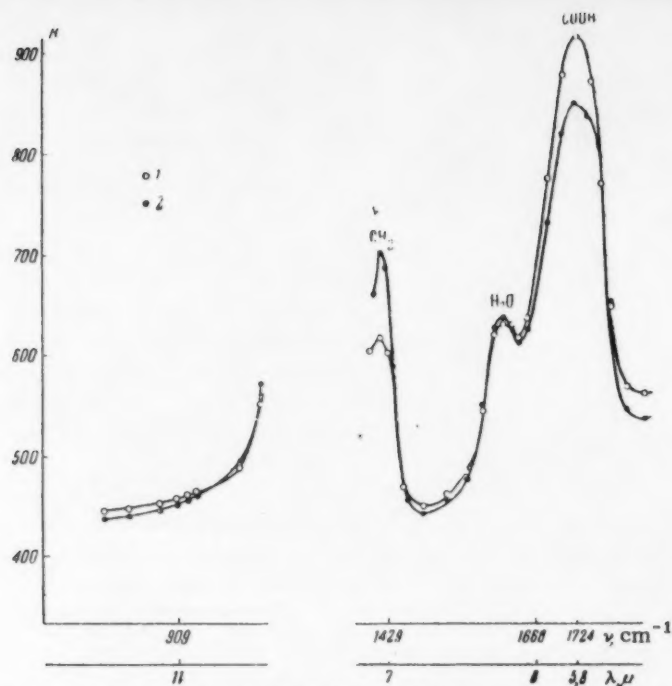


Fig. 3. Absorption spectra of dialdehydocelluloses oxidized with nitrogen oxides. Content of carboxyl groups: 1) 1.163; 2) 0.97 g-equiv. per 100 g of sample.

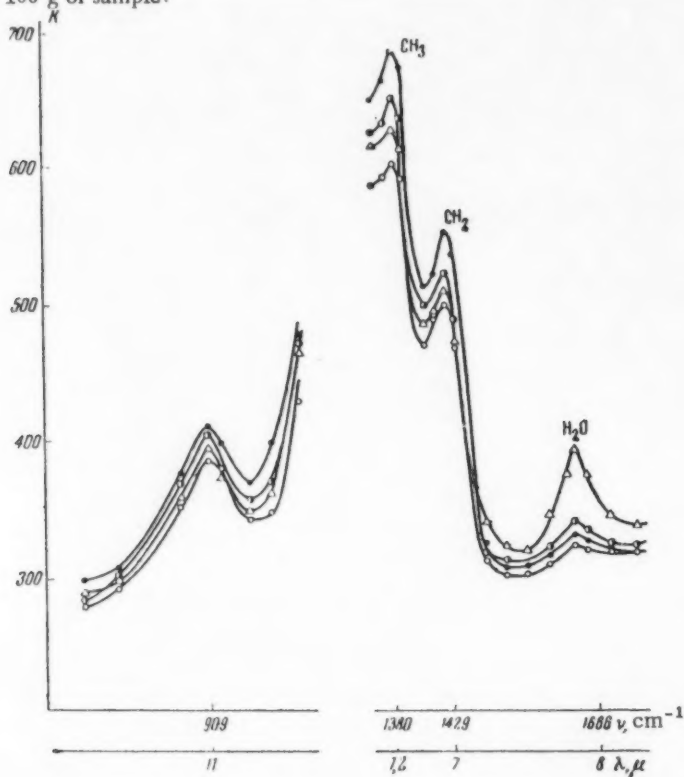


Fig. 4. Absorption spectra of dialdehydocelluloses treated with a methanol solution of HCl. The symbols and content of aldehyde groups are the same as in Fig. 1.

absorption at $11\ \mu$ increases with an increase in the content of aldehyde groups. The fact that the absorption band at $11\ \mu$ belongs to aldehyde groups in a bound state is confirmed by data presented in Fig. 2. The data in this figure show that there is a sharp decrease in the intensity of the band at $11\ \mu$ and an appreciable increase in that at $5.8\ \mu$ when dialdehydocellulose is oxidized with sodium chlorite. Oxidation of the same dialdehydocelluloses with nitrogen oxides was accompanied by practically complete disappearance of the absorption band at $11\ \mu$ (Fig. 3).

The absorption spectra of products from the reaction of dialdehydocelluloses with a methanol solution of HCl at 70° (Fig. 4) also show a considerable fall in the intensity of the band at $11\ \mu$ with a simultaneous increase in the absorption band characteristic of CH_3 groups. These results agree with literature data [17]. The data presented above indicate that the absorption band at $11\ \mu$ is caused by aldehyde groups in a bound state and changes as a result of chemical conversions of these groups during oxidation and methylation.

SUMMARY

1. Dialdehydocellulose does not absorb in the region of $5.8\ \mu$, which is characteristic of $\text{C}=\text{O}$ groups, and this confirms that the aldehyde groups in these preparations are in a changed state.
2. The intensity of the absorption at $11\ \mu$ increases with an increase in the number of glucose units of the cellulose molecule oxidized to aldehydes.
3. The intensity of the absorption at $11\ \mu$ decreases with the disappearance of the aldehyde groups as a result of their oxidation to carboxyl groups or as a result of treatment of the dialdehydocelluloses under conditions where gem-hydroxyls are methylated.
4. The facts listed indicate that the absorption band at $11\ \mu$ should be assigned to symmetrical vibrations of the hemiacetal bond.

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THERMODYNAMIC ACTIVITY OF WATER IN THE SYSTEM $H_2O - H_2SO_4 - i-C_3H_7OH$

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

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The partial vapor pressure of water over alcohol-water solutions of acids has not been measured. Available literature data [1] refer to the total pressure of the system $H_2O - H_2SO_4 - i-C_3H_7OH$. Nonetheless, this value is an important characteristic of the thermodynamic state of water in the solution. A knowledge of the vapor pressure of water over a system makes it possible to calculate its activity.

EXPERIMENTAL

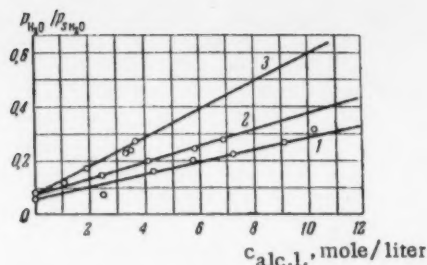
We measured the partial vapor pressures of water and alcohol over solutions of isopropanol in 68.06% H_2SO_4 at 30, 40, and 50°. The experimental procedure was as follows. Acid of the required concentration was introduced into a 500 cc reaction flask. The air was pumped from the system and a definite water vapor pressure, corresponding to the concentration of the acid taken, was established. The reaction flask was thermostatted and the liquid in

Activities of Water in the System $H_2O - H_2SO_4 - i-C_3H_7OH - i-C_3H_7SO_4H$ (starting H_2SO_4 concentration H_2SO_4 $c_{H_2SO_4} = 68.06\%$ H_2SO_4)

Temp. °C	$c_{H_2SO_4}^*$ %	$c_{H_2SO_4}^*$ mole/liter	$c_{alk.ac.}^*$ mole/liter	$c_{alc.l.}^*$ mole/liter	$c_{CH_3F \cdot 10}^*$ mole/liter	$P_{H_2O}^*$ mm Hg	p/p_{H_2O}	a_{H_2O}
50	68,06	11,01	0,000	0,000	0,000	7,20	0,0778	4,319
50	66,82	10,747	0,263	1,035	0,255	10,90	0,1176	6,528
50	65,42	10,44	0,570	1,900	0,879	15,97	0,1725	9,575
50	63,20	9,93	1,080	3,326	0,949	21,9	0,2367	13,139
50	63,60	9,99	1,020	3,522	1,037	22,14	0,2392	13,278
50	63,10	9,91	1,100	3,66	1,916	25,24	0,2727	15,137
40	68,06	11,01	0,000	0,000	0,000	3,8	0,0687	3,813
40	64,10	10,133	0,877	2,456	0,248	8,21	0,1484	8,237
40	61,8r	9,578	1,432	4,043	1,705	10,99	0,1986	11,024
40	59,1	8,982	2,028	5,780	2,832	13,60	0,2458	13,644
40	57,40	8,61	2,400	6,867	3,668	15,20	0,2747	15,248
30	68,06	11,01	0,000	0,000	0,000	2,0	0,0609	3,380
30	63,40	9,962	1,048	2,518	0,445	2,45	0,0746	4,141
30	60,50	9,296	1,714	4,285	0,668	5,37	0,1635	9,076
30	58,30	8,796	2,214	5,754	2,260	6,87	0,2081	11,551
30	55,73	8,288	2,722	7,186	3,674	7,46	0,2273	12,617
30	53,80	7,89	3,120	9,100	5,393	8,77	0,2672	14,832
30	53,00	7,73	3,280	10,200	6,410	10,38	0,3162	17,552

*Equilibrium concentrations of mixture components.

it stirred with a magnetic stirrer. Then an ampoule of alcohol was broken under the acid layer by means of a suitable device. After a certain time which was necessary for equilibrium to be reached between the alcohol and the acid, the reaction flask was connected to a large vessel (11374.26 cc in volume) and the pressure change in the system followed by means of an oil manometer. When equilibrium had been established between the liquid and the gas phase (no further pressure change in the system), the large vessel was shut off from the reaction flask. The mixture of H_2O and $i-C_3H_7OH$ vapors present in the large vessel was frozen in a trap and analyzed for alcohol content.



Graphs for calculating the parameters \bar{m} and \bar{n} of equation (2): 1) 30°; 2) 40°; 3) 50°.

given in the last column of the table. The data obtained are described well by a simple empirical relation of the following form:

$$\alpha_{H_2O} = 55.51 m(c_{alc.l.} + n) \quad (2)$$

The parameters \bar{m} and \bar{n} in equation (2) were calculated by means of a graph in the coordinates $p_{H_2O}/p_{SH_2O} - c_{alc.l.}$ (Fig. 1). 30° $\bar{m} = 2.19 \cdot 10^{-2}$ liter/mole; $\bar{n} = 2.783$ mole/liter, 40° $\bar{m} = 2.98 \cdot 10^{-2}$ liter/mole; $\bar{n} = 2.307$ mole/liter, 50° $\bar{m} = 5.42 \cdot 10^{-2}$ liter/mole; $\bar{n} = 1.435$ mole/liter.

The increase in the activity of water in the system with an increase in the alcohol concentration is evidently connected with the destruction of large complexes of water molecules formed through hydrogen bonds [4-6]. The number of free water molecules increases as a result of the addition of alcohol and this leads to an increase in the activity of water.

SUMMARY

1. The partial vapor pressures of water and alcohol over solutions of isopropanol in 68% H_2SO_4 at 30, 40, and 50° were measured.
2. An empirical formula is given for calculating the activity of water in solutions of $i-C_3H_7OH$ in 68% H_2SO_4 at 30, 40, and 50°.

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EQUILIBRIUM OXIDATIONS OF FERROCENE AND RUTHENOCENE WITH IODINE

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In order to determine the thermodynamic characteristics (ΔF , ΔH , and ΔS) of the oxidation of ferrocene [1] and ruthenocene with iodine, in the present work, we studied the absorption spectra of the ternary systems $\text{Fc}-\text{I}_2$ - C_6H_6 and $\text{Rc}-\text{I}_2$ - C_6H_6 * in the region of 350-420 m μ . In the opinion of some authors [2], ruthenocene should have a high resistance to oxidation. However, the results of a polarographic investigation [3] contradicted this hypothesis as the reaction $\text{Fc}^+ + \text{Rc} = \text{Fc} + \text{Rc}^+$ in 90% alcohol has a negative value for ΔF , equal to -1.5 kcal/mole.

EXPERIMENTAL

Iodine sublimed by the usual method and ferrocene and ruthenocene purified by vacuum sublimation were used in the experiments. The benzene for the experiments was repeatedly frozen and distilled. The measurements were made on an SF4 instrument and partly on an SF2M at various temperatures in a thermostatted glass cell ($d = 4.33$ cm). The two instruments gave similar results.

The system $\text{Fc}-\text{I}_2-\text{C}_6\text{H}_6$ was investigated previously [4] by Brand and Snedden under analogous conditions. The experimental data were interpreted with the hypothesis that the only reaction product is FcI_3 . It was also established that crystalline FcI_5 is formed when hexane solutions of ferrocene and iodine are mixed. This gave us grounds for assuming that there is a possibility of FcI_5 existing in benzene solution also. In the present work we determined the deviation of the optical density D from the additive value D_0 at various wavelengths. Figure 1 gives curves obtained on the basis of these data and also the absorption spectrum of $(\text{CH}_3)_3\text{C}_6\text{H}_5\text{NI}_3$ with the optical density of the triiodide ion as the standard. The spectrum of the latter is known to depend little on either the solvent [5] or the cation with which it forms an ion pair.

For equilibrium in the reactions



the relation of $D-D_0$ to $[\text{Fc}]$ and $[\text{I}_2]$ should have the following form:

$$(D - D_0) [\text{Fc}]^{-1} [\text{I}_2]^{-3/2} = \Delta \epsilon_{\text{FcI}_3} K_1 + \Delta \epsilon_{\text{FcI}_5} K_2 [\text{I}_2],$$

where D is the optical density of the solution at equilibrium,

$$D_0 = \epsilon_{\text{Fc}} [\text{Fc}]_0 + \epsilon_{\text{I}_2} [\text{I}_2]_0, \quad \Delta \epsilon_{\text{FcI}_3} = \epsilon_{\text{FcI}_3} - \epsilon_{\text{Fc}} - \frac{3}{2} \epsilon_{\text{I}_2},$$

$\Delta \epsilon_{\text{FcI}_5} = \epsilon_{\text{FcI}_5} - \epsilon_{\text{Fc}} - \frac{5}{2} \epsilon_{\text{I}_2}$; K_1 and K_2 are the equilibrium constants, and ϵ are the molar extinction coefficients. In this equation, the concentrations $[\text{Fc}]$ and $[\text{I}_2]$ may be replaced by the initial concentrations as the concentration of the reaction product is very low under the experimental conditions [4]. In addition, it may also be assumed that $\Delta \epsilon_{\text{FcI}_3} = \epsilon_{\text{FcI}_3}$ and $\Delta \epsilon_{\text{FcI}_5} = \epsilon_{\text{FcI}_5}$ due to the low values of ϵ_{Fc} and ϵ_{I_2} over the range of wavelengths investigated. Experiment showed (Fig. 2) that there is the linear relation $(D-D_0) [\text{Fc}]_0^{-1} [\text{I}_2]_0^{-3/2} = a + b [\text{I}_2]_0$, where a and b are empirical constants. A relation of an analogous character is observed in the system $\text{Rc}-\text{I}_2-\text{C}_6\text{H}_6$ (Fig. 3). If the hypothesis that reactions (1) and (2) occur is correct, then $a = \epsilon_{\text{FcI}_3} K_1$ and $b = \epsilon_{\text{FcI}_5} K_2$. Hence, it follows that

*The following arbitrary symbols are used in the article: $\text{Fc}-(\text{C}_5\text{H}_5)_2\text{Fe}$, $\text{Rc}-(\text{C}_5\text{H}_5)_2\text{Ru}$ and Mc -dicyclopentadienyl metal $(\text{C}_5\text{H}_5)_2\text{Me}$.

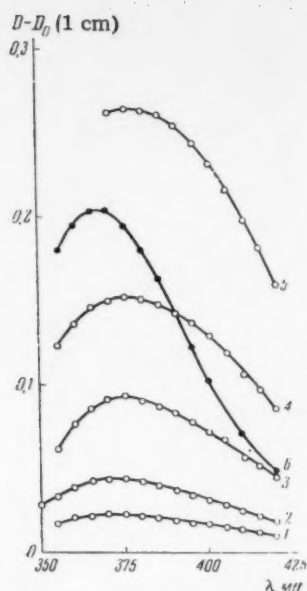


Fig. 1. The system ferrocene-iodine-benzene at 7.5° with the concentrations in 10^{-3} mole/liter: 1) $[I_2]_0 = 0.38$; $[Fc]_0 = 0.44$; 2) $[I_2]_0 = 0.38$; $[Fc]_0 = 0.88$; 3) $[I_2]_0 = 0.56$; $[Fc]_0 = 0.88$; 4) $[I_2]_0 = 0.75$; $[Fc]_0 = 0.88$; 5) $[I_2]_0 = 1.112$; $[Fc]_0 = 0.66$; 6) $(CH_3)_3C_6H_5NI_3$ in benzene at 18° ($7.4 \cdot 10^{-6}$ mole/liter).

We established that equilibrium in the oxidation of ferrocene by iodine in benzene is reached after ~ 1 hr at 7.5° with reagent concentrations of $5 \cdot 10^{-4}$ mole/liter. Ruthenocene is oxidized practically instantaneously under analogous conditions. It may be assumed that the slowest stage of the reaction is the transfer of an electron $Mc + I_2 = McI + I$ or $Mc + 2I_2 = McI_3 + I$. The observed differences in the rates of oxidation of ferrocene and ruthenocene may be explained if it is assumed that the activation energy is determined by ΔH of the transfer of an electron. For the process $Mc + 2I_2 = McI_3 + I$, this value may be found as the sum of ΔH for the reactions $Mc + \frac{3}{2} I_2 = McI_3$ and $\frac{1}{2} I_2 = I$. Calculation shows that the transfer of an electron is weakly endothermic and in the case of ruthenocene, ΔH is 1.5 kcal/mole less than in the case of ferrocene.

TABLE 1. Equilibrium Constants for the Reactions $Mc + \frac{3}{2} I_2 = McI_3$ (K_1) and $Mc + \frac{5}{2} I_2 = McI_5$ (K_2)

Temp. °C	$K_1, \text{mole}^{-3/2} \cdot \text{liter}^{3/2}$		$K_2, 10^{-4} \text{mole}^{-5/2} \cdot \text{liter}^{5/2}$	
	(Mc-Fc)	(Mc-Rc)	(Mc-Fc)	(Mc-Rc)
7,5	201	373	12,9	82
15,0	132	185	6,3	39
20,0	97	150	3,7	19
25,0	70,5	104	2,75	11,6
35,0	41	63	1,18	3,4

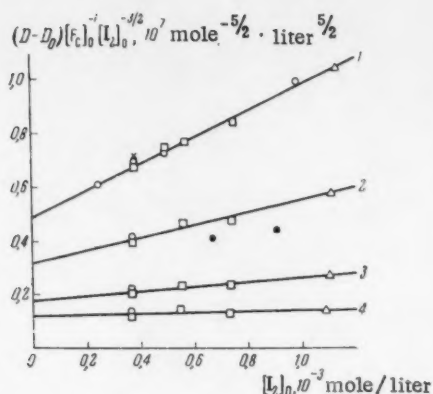


Fig. 2. The system ferrocene-iodine-benzene: 1) 7.5°; 2) 15.0°; 3) 25.0°; 4) 35.0°; $[Fc]_0$ in 10^{-3} mole/liter, 0.24 (x); 0.44 (O); 0.66 (Δ); 0.88 (□); O—literature data [4] at $20 \pm 2^\circ$.

the relations of \underline{a} and \underline{b} to λ at constant temperature should be determined by the values $\epsilon_{FcI_3} K_1$ and $\epsilon_{FcI_5} K_2$. A comparison of these relations with the absorption spectra of $(CH_3)_3C_6H_5NI_3$ and $(CH_3)_3C_6H_5NI_5$ (Fig. 4) confirms the hypothesis on the formation of FcI_3 and FcI_5 .

The equilibrium constants at various temperatures were found from the corresponding values of the constants \underline{a} and \underline{b} . The extinction coefficients of the tri- and penta-iodides were taken as equal to $\epsilon_{(CH_3)_3C_6H_5NI_3}$ and $\epsilon_{(CH_3)_3C_6H_5NI_5}$. The values of K_1 and K_2 are given in Table 1 and the values of ΔF , ΔH , and ΔS in Table 2.

TABLE 2. Thermodynamic Data for the Reactions Under Standard Conditions (25°)

Reaction	ΔF , kcal per mole	ΔH , kcal per mole	ΔS , entropy units
$Fc + \frac{3}{2} I_2 = FcI_3$	-2,52	-10	-25
$Rc + \frac{3}{2} I_2 = RcI_3$	-2,75	-11,5	-30
$Fc + \frac{5}{2} I_2 = FcI_5$	-6,05	-15	-30
$Rc + \frac{5}{2} I_2 = RcI_5$	-6,90	-19	-41
$FcI_3 + I_2 = FcI_5$	-3,53	-5	-5
$RcI_3 + I_2 = RcI_5$	-4,15	-7,5	-11

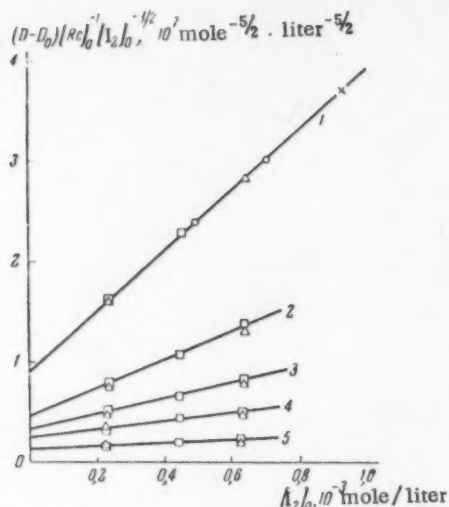


Fig. 3. The system ruthenocene-iodine-benzene: 1) 7.5°; 2) 15.0°; 3) 20.0°; 4) 25.0°; 5) 35.0°; [Fc] in 10^{-3} mole/liter; 0.09 (x); 0.23 (O) 0.35 (Δ); 1.15 (\square).

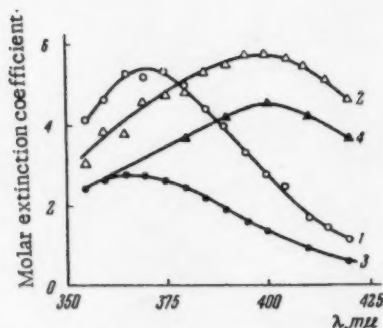


Fig. 4. The system ferrocene-iodine-benzene at 7.5°: 1) \bar{a} in 10^6 mole $^{-5/2}$ · liter $^{5/2}$; 2) \bar{b} in 10^9 mole $^{-7/2}$ · liter $^{7/2}$; 3) $\epsilon(\text{CH}_3)_3\text{C}_6\text{H}_5\text{NI}_3$ and 4) $\epsilon(\text{CH}_2)_3\text{C}_6\text{H}_5\text{NI}_5$ in 10^{-4} mole $^{-1}$ · liter · cm $^{-1}$ in benzene at 18°.

From the data in Table 2 it is possible to determine the value of ΔH for the reaction $\text{Rc} + \text{FcI}_3 = \text{RcI}_3 + \text{Fc}$ in benzene which equals -1.5 kcal/mole in this case. The comparatively low value of ΔH indicates similar ionization potentials for ferrocene and ruthenocene. This indicates that the ionization potential of ruthenocene is close to 7 eV as the ionization potential of ferrocene is known to equal 7.05 eV [6]. Ruthenocene is thermodynamically more stable than ferrocene. It is known [7] that the heats of formation by the reaction $\text{Me}(1) + 2\text{C}_2\text{H}_5(\text{g}) = \text{Me}(\text{C}_2\text{H}_5)_2(\text{g})$, calculated from thermochemical data, equalled 147 (Me = Fe) and 187 (Me = Ru) kcal/mole. An investigation of the infrared spectra of the two compounds [8] indicates that the bond of the metal with the ring is stronger in the ruthenocene molecule. These data and the similar values of the ionization potentials indicate that the ruthenocinium cation is thermodynamically more stable than the ferrocinium cation.

SUMMARY

The thermodynamic characteristics (ΔF , ΔH , and ΔS) of the formation of ferrocinium and ruthenocinium tri- and penta-iodides were measured.

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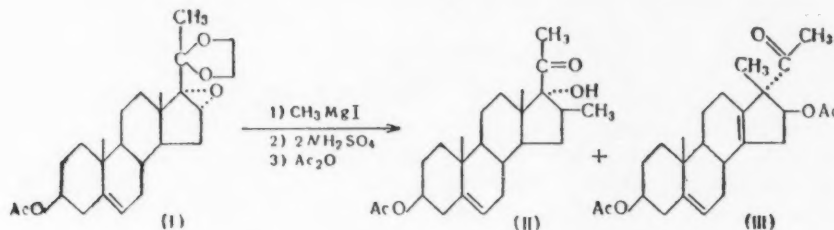
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REACTION OF METHYLMAGNESIUM IODIDE WITH STEROID KETO OXIDES

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16 α -Methyl-9 α -fluoro- Δ^1 -dehydrocortisol ("dexamethazone") is the most active analog of cortisone at the present time [1, 3]. According to literature data, the corresponding 16 β -methyl derivative has an analogous activity [2]. During our work on the synthesis of these compounds, we studied the reaction of methylmagnesium iodide with the 3-acetate of the 20-ketal of 16 α ,17 β -oxido- Δ^5 -pregnenol-3 β -one-20 (I). Heating the latter with CH_3MgI etherate in benzene to 88-90° formed an oily product, hydrolysis and subsequent acetylation of which yielded two substances: a monoacetate (II) with m.p. 150-152° and a diacetate (III) with m.p. 214-216°. Hydrolysis of the monoacetate (II) gave (IV) with m.p. 238-240°. On the basis of elementary analysis, the infrared spectrum, and general considerations on the stereochemistry of the opening of the α -oxide ring in steroids, substance (IV) was assigned the structure of 16 β -methyl- Δ^5 -pregnenediol-3 β ,17 α -one-20 and for demonstration of this structure, the substance was hydrogenated over a palladium catalyst to the corresponding derivative of allopregnane (V). A comparison of the molecular rotation of (V) $M = 82.93$ with that of the known 16 α -epimer [3] $M = +41.46$ indicates 16 β -methyl- Δ^5 -pregnenol-3 β -one-20 [4, 5] was hydrogenated over PtO_2 to the corresponding allo product, which was converted through the enol acetate and the 17,20-oxide to 16 β -methylallopregnenediol-3 β ,17 α -one-20 by Gallagher's method. The latter was found to be identical with the (V) we obtained previously. Hydrolysis of the second reaction product (III) gave 18-nor-17 β -methyl-17-iso- Δ^5 -pregnadienediol-3 β ,16 β -one-20 (VI), whose structure was also demonstrated by synthesis [6]. The formation of (VI) was evidently connected with a Wagner-Meerwein rearrangement [6, 7].



EXPERIMENTAL

Reaction of methylmagnesium iodide with (I). A solution of 5 g of (I) in 200 ml of dry benzene was added dropwise with stirring to the Grignard reagent, prepared by the usual method from 5 g of Mg turnings, 50 ml of dry ether, and 15 ml of methyl iodide. The reaction was continued for 10 hr. An oily reaction product was isolated and after hydrolysis and acetylation, this gave two substances: the first was the 3-acetate of 16 β -methyl- Δ^5 -pregnenediol-3 β ,17 α -one-20 (II) with m.p. 150-152°; $[\alpha]_D^{20} = -30.15$ ($c = 0.2$ dioxane); λ_{max} 3.01; 5.88; 5.76 μ . Found: C 74.09; H 9.00; Ac 13.00%. $\text{C}_{24}\text{H}_{36}\text{O}_4$. Calculated %: C 74.19; H 9.33; Ac 11.10%. The second substance was the 3,16-diacetate of 18-nor-17 β -methyl-17-iso- Δ^5 -pregnadienediol-3 β ,16 β -one-20 (III) with m.p. 214-216°; $[\alpha]_D^{20} = 15.6$ ($c = 1$, chloroform); λ_{max} 5.72; 5.75; 5.92 μ . Found: C 72.24; H 8.25; Ac 20.30%. $\text{C}_{24}\text{H}_{34}\text{O}_5$. Calculated: C 72.40; H 8.30; Ac 19.98%.

Hydrolysis of (II) and (III) and preparation of (IV) and (VI). Acid hydrolysis of the acetate (II) and diacetate (III) gave 16 β -methyl- Δ^5 -pregnenediol-3 β ,17 α -one-20 (IV) with m.p. 238-240°; $[\alpha]^{20}_D = -42.0^\circ$ (c = 0.2, dioxane); λ_{\max} 3.00; 2.98; 5.92 μ . Found: C 76.10; H 9.68%. $C_{22}H_{34}O_3$. Calculated: C 76.25; H 9.89%. Acid hydrolysis of the diacetate (III) gave 18-nor-17 β -methyl-17-iso- $\Delta^{5,13}$ -pregnadienediol-3 β ,16 β -one-20 (VI) with m.p. 188-190°; $[\alpha]^{20}_D = -128.25^\circ$ (c = 1.0, chloroform); λ_{\max} 2.94; 3.04; 5.90 μ . Found: C 76.32; H 9.42%. $C_{21}H_{30}O_3$. Calculated: C 76.35; H 9.10%.

Hydrogenation of (IV). A 0.4-g sample of (IV) was dissolved in 20 ml of dioxane and 20 ml of glacial acetic acid. The substance was hydrogenated over 0.05 g of Pd/CaCO₃ for 1.5 hr. We isolated 0.35 g of 16 β -methylallopregnanediol-3 β ,17 α -one-20 (V) with m.p. 244-245°; $[\alpha]^{20}_D = -23.8^\circ$ (c = 0.2, dioxane); λ_{\max} 3.00; 2.96; 5.87 μ ; $M_D = -82.93^\circ$. Found: C 76.03; H 10.23%. $C_{22}H_{36}O_3$. Calculated: C 75.82; H 10.41%.

Synthesis of 16 β -methylallopregnanediol-3 β ,17 α -one-20. A 1.5-g sample of 16 β -methyl- Δ^5 -pregnenol-3 β -one-20 with m.p. 196-197° (obtained from dehydropregnenolone with diazomethane through the corresponding pyrazoline derivative) was dissolved in 50 ml of dioxane and 20 ml of glacial acetic acid and hydrogenated in the presence of PtO₂. We obtained 16 β -methylallopregnanol-2 β -one-20 with m.p. 194-196°; λ_{\max} 3.02; 5.88 μ . The product was acetylated with acetic anhydride in pyridine and without purification, the acetate was enolized by boiling with acetic anhydride in toluene in the presence of sulfosalicylic acid. The product was then oxidized with monoperphthalic acid and hydrolyzed with 2% NaOH solution. We isolated 16 β -methylallopregnanediol-3 β ,17 α -one-20 with m.p. 243-245°; $[\alpha]^{20}_D = -24^\circ$ (c = 0.2, dioxane). A mixed melting point of this substance with that we obtained previously was not depressed. The infrared spectra were identical.

Synthesis of 18-nor-17 β -methyl-17-iso- $\Delta^{5,13}$ -pregnadienediol-3 β ,16 β -one-20. The 3-acetate of the 10-ketal of 16 α ,17 α -oxido- Δ^5 -pregnenol-3 β -one-20 (I) was boiled with acetic anhydride. We isolated the 3,16-diacetate of 18-nor-17 β -methyl-17-iso- $\Delta^{5,13}$ -pregnadienediol-3 β ,16 β -one-20 with m.p. 214-216°; $[\alpha]^{20}_D = -10^\circ$ (c = 1, chloroform). Acid hydrolysis yielded 18-nor-17 β -methyl-17-iso- $\Delta^{5,13}$ -pregnadienediol-3 β ,16 β -one-20 with m.p. 189-190°; $[\alpha]^{20}_D = -130^\circ$ (c = 1, chloroform). Neither of the substances obtained depressed the melting points of the samples we obtained previously. The infrared spectra were found to be identical.

SUMMARY

The reaction of the 3-acetate of the 20-ketal of 16 α ,17 α -oxido- Δ^5 -pregnenol-3 β -one-20 with methylmagnesium iodide and subsequent hydrolysis of the reaction product yielded 16 β -methyl- Δ^5 -pregnenediol-3 β -17 α -one-20. 18-Nor-17 β -methyl-17-iso- $\Delta^{5,11}$ -pregnadienediol-3 β ,16 β -one-20 was formed as a by-product.

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RATE OF HYDROGENATION OF VINYL
AND ALLYL COMPOUNDS OF CARBON, SILICON,
GERMANIUM, AND TIN ON SKELETAL NICKEL

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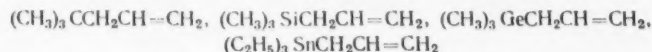
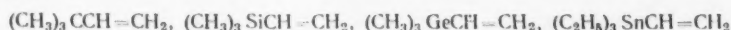
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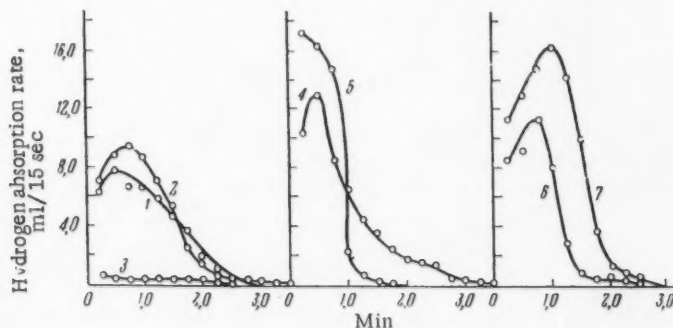
In ionic reactions, the rate of addition (of thiocyanogen, for example) to the double bond of compounds of the type $R_3MCH=CH^2$ (where $M = C, Si, Ge$, and Sn) is known [1] to increase from carbon to tin in the following order: $C < Si < Ge < Sn$. In radical processes (polymerization), the reactivity of the same compounds [2] depends differently on the nature of the atom M : $Si > C > Ge > Sn$.

EXPERIMENTAL

Using hydrogenation as the example, in the present work we studied the reactivity of α - and β -ethylenic bonds in the compounds:



The skeletal nickel catalyst used in the work was prepared by extracting Ni-Al alloy (1 : 1) with 20% sodium hydroxide. The catalyst was weighed on torsion balances in alcohol. The experiments were carried out in a hydrogenation flask with vigorous mixing (700-800 shakes per min). Equimolecular amounts of the compounds corresponding to a consumption of ~ 50 ml of hydrogen were used in the reaction. The reaction rate was characterized by the rate of hydrogen absorption with time, which is shown in the figure, and the half reaction period $\tau/2$, which is given in the table. Readings were taken every 15 sec. The table shows that the hydrogenation rate of vinyl compounds falls from silicon to germanium and carbon; their values of $\tau/2$ were 25, 32, and 65 sec, respectively. Vinyltriethyltin was hydrogenated very slowly; the hydrogen absorption rate did not exceed 0.3 ml/sec (experiments 1, 3,



5, and 7). As can be seen, the reactivity of the vinyl group in catalytic hydrogenation depends substantially on the nature of the atom to which it is attached. The rate of saturation of the allyl group also depends on the nature of the atom to which it is attached. In this case also the rate of addition of hydrogen falls from silicon and germanium

Skeletal Nickel 0.1 g; 96% Ethanol, 10 ml

Expt. No.	Compound hydrogenated	Amt. of substance, g	Hydrogen consumption, ml		Hydrogenation rate as $\tau/2$, sec.	Constants of starting materials		
			theoretical	actual		b.p., °C (p, mm Hg)	n_D^{20}	d_4^{20}
1	$(CH_3)_3CCH=CH_2$	0,1909	50,8	40,0	65	41,2(760)	1,3770	0,6529
2	$(CH_3)_3CCH_2CH=CH_2$	0,2598	58,0	50,7	58	72(745)	1,3914	0,6827
3	$(CH_3)_3SiCH=CH_2$	0,2310	51,0	47,5	25	54,6(744)	1,3910	0,6903
4	$(CH_3)_3SiCH_2-CH=CH_2$	0,2652	51,0	47,5	41	85,4(752)	1,4075	0,7195
5	$(CH_3)_3GeCH=CH_2$	0,3092	48,0	40,0	32	70,6(735)	1,4153	0,9970
6	$(CH_3)_3GeCH_2-CH=CH_2$	0,3581	50,8	41,6	41	101(764)	1,4333	0,9952
7	$(C_2H_5)_3SnCH=CH_2$	0,5315	51,1	*	*	174(750)	1,4780	1,2133
8	$(C_2H_5)_3SnCH_2CH=CH_2$	0,5566	50,5	0	0	63(5)	1,4903	1,2231

*The reaction was not completed because of the low hydrogenation rate.

to carbon; their values of $\tau/2$ were 41.41 and 58 sec, respectively. However, allyltriethyltin was not hydrogenated at all on the skeletal nickel catalyst (Expts. 2, 4, 6, and 8). The reactivity of the double bond also depends on its position relative to the heteroatom. The table and figure show that vinyl compounds of silicon, germanium, and tin are hydrogenated more rapidly than the corresponding allyl derivatives (Expts. 3, 5, and 7, and 4, 6, and 8, and curves 3, 5, and 7, and 4 and 6). The carbon compounds showed the reverse relation, i.e., vinyltrimethylmethane was hydrogenated more slowly than allyltrimethylmethane (Expts. 1 and 2 and curves 1 and 2). In this connection it is interesting to note that the reactivity of vinylsilanes in radical additions is much greater than that of allylsilanes [3-5], while allylsilanes are more reactive than vinylsilanes in ionic reactions [6].

SUMMARY

1. The rate of hydrogenation of compounds of the type $(CH_3)_3MCH=CH_2$ and $(CH_3)_3MCH_2CH=CH_2$, where M is C, Si, Ge, and Sn, on a skeletal nickel catalyst falls in approximately the same order as the reactivity of these compounds in radical polymerization: $Si > Ge > C > Sn$.

As in radical additions, vinyl compounds of silicon are hydrogenated more rapidly than allyl compounds. Vinyl and allyl double bonds in germanium and tin compounds behave analogously, while carbon compounds show the reverse relation.

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SYSTEMATIZATION OF TYPES OF TRIPLE BOND

A. T. Balaban

Institute of Atomic Physics, Bucharest

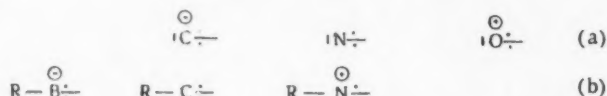
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 12, pp. 2060-2061, December, 1960

Original article submitted June 20, 1960

The exceptional stability of the homodiatom molecule N_2 is caused by the electronic configuration of the completed level $KK (2\sigma)^2 (2\sigma)^2 (2\pi)^4 [1]$, in which all the bonding molecular orbitals are filled. The heterodiatom molecule CO, which like N_2 is formed from any chemical compound containing the corresponding atoms at temperatures above 1000° , has an analogous electronic configuration. There are other molecules formed from any chemical compound at very high temperatures: HCN, C_2H_2 , and NO. All these molecules have a triple bond (however, NO has a particular type of bond) and because of their high thermal stability, they are used to reach temperatures above 5000° [2]. Thus, it may be assumed that there are three types of completed electronic configurations in compounds of elements of the first short period: an octet of σ -electrons in saturated compounds with sp^3 hybridization (e.g., methane and diamond), an aromatic sextet of π -electrons with sp^2 hybridization (e.g., benzene and graphite), and a third type, whose occurrence is not yet generally accepted, namely, a quarter of π -electrons in molecules with a triple bond and sp hybridization (e.g., N_2).

All known and also some unknown molecules with a triple bond may be derived by combination of the following types of atoms in pairs:



(The points denote π -electrons, the vertical line denotes p-electrons, and the horizontal line σ -electrons; see also [3, 4].) Only molecules and ions formed by combination of atoms of type (a) (first line) have the electronic configuration of a completed level. Molecules and ions containing atoms of type (b) (second line) do not have p-orbitals and do not have the high stability of the previous molecules (the fact that the p-orbitals of N_2 and CO participate in the molecular bond follows from the complete or almost complete absence of basicity of these molecules

$N \vdots \vdots N$ and $\ominus C \vdots \vdots \ominus$ are not completely satisfactory). On the basis of these arguments, we propose that: 1) the unusual acidity of acetylene or hydrocyanic acid is not caused only by an increase in the fraction of the s-orbitals in the hybrid or polarization of the atoms [5], but largely by the fact that as a result of ionization the ions $\ominus C \vdots \vdots C \vdots \vdots \ominus$ and $\ominus C \vdots \vdots N \vdots \vdots$ are formed with an electronic configuration analogous to that of nitrogen and that 2) the formation of acetylene and hydrocyanic acid at high temperature is not caused exclusively by the endothermal nature of their formation reactions, but by the formation of the same ions in the gas phase (or $N \vdots \vdots O \vdots \vdots \oplus$ in the case of NO synthesis). The latter hypothesis could be checked by mass spectrometric analysis of the gases formed during the preparation of HCN by Andrusov's method or C_2H_2 by cracking methane.

Of the unknown molecules with a triple bond predicted on the basis of the systematization proposed, the most interesting are molecules containing boron. Goubeau [6] proposed that in the case of boron compounds, bond orders higher than two are not obtained because of the low electronegativity of boron. Another reason could be the fact that all the conceivable boron compounds with a triple bond are of the type $K - B \vdots \vdots$ [see line (b)], which cannot have a completed electronic configuration.

The triple bond in molecules containing atoms that differ strongly in electronegativity, such as $\ominus B \vdots \vdots F \vdots \vdots \oplus$ [7], are also unstable. The question arises as to whether the molecular ion $\oplus O \vdots \vdots O \vdots \vdots \oplus$ is stable despite the fact

that it bears two charges and that the type of atom O^{2+} has a very high electronegativity. The successive ionization potentials of the O_2 molecule [8, 9] do not confirm this stability. This problem could be solved with the aid of the mass spectrum of oxygen enriched in O^{18} at an ionization potential above 50 v; if the ions O_2^{2+} are stable, then one would expect a peak of corresponding intensity at $m/e = 17$, caused by the particles $\text{O}^{18} \text{O}^{18}$.

I would like to thank V. N. Kondrat'ev and M. I. Vinnik for valuable comments.

SUMMARY

All known compounds with a triple bond may be divided into two types. The first type consists of molecules and ions with the electronic configuration of a completed layer. The triple bond in these compounds has a high strength. The second type consists of molecules and ions formed by atoms that do not have p-orbitals and this causes the instability of this type of triple bond.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

COMMENTS ON PROF. V. K. SEMENCHENKO' ARTICLE

"TWO LIMITING CASES OF THERMODYNAMIC EQUILIBRIUM" *

V. N. Masyukov and L. M. Tsukernik

All-Union Scientific Research Institute of the Mechanization of Agriculture

Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 12, p. 2262, December, 1960

Original article submitted March 29, 1960, revised September 26, 1960

In the article mentioned, which was published in No. 2 of your journal in 1959 (p. 368), Prof. V. K. Semenchenko attempted to demonstrate that Nernst's theorem stems from the first and second principles of thermodynamics with the condition of the maximum stability of the thermodynamic equilibrium of the system. It seems to us that before investigating the limiting case of $D \rightarrow \infty$, the author should demonstrate, without using Nernst's theorem, that this case has physical meaning. Were the author able to find such a demonstration, it would mean that he was actually able to show that Nernst's theorem is a consequence of the first two principles of thermodynamics. However, the author arbitrarily adopted the condition $D \rightarrow \infty$, which is equivalent to $T/c_v \rightarrow \infty$, that essentially already predetermines the inaccessibility of absolute zero. Having set the condition $D \rightarrow \infty$, Prof. V. K. Semenchenko naturally arrives at the fact that

$$\left(\frac{\partial T}{\partial v}\right)_p \rightarrow \infty; \quad \left(\frac{\partial p}{\partial v}\right)_T = \left(\frac{\partial p}{\partial v}\right)_s; \quad s_0 \rightarrow 0,$$

i.e., the known entropy interpretation of the same theorem.

Thus, V. K. Semenchenko's calculations cannot be regarded as a demonstration of the fact that the Nernst theorem follows from the first two principles of thermodynamics since the arbitrarily adopted condition that $D \rightarrow \infty$ does not follow from either the first or the second principle of thermodynamics and has not been demonstrated by the author. In our opinion, it is impossible to demonstrate that the limiting case when $D \rightarrow \infty$ can have a real physical meaning starting only from the first two principles of thermodynamics and the condition of the stability of the thermodynamic equilibrium of the system.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY
ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashglz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroilzdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab. - Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. - Publisher.

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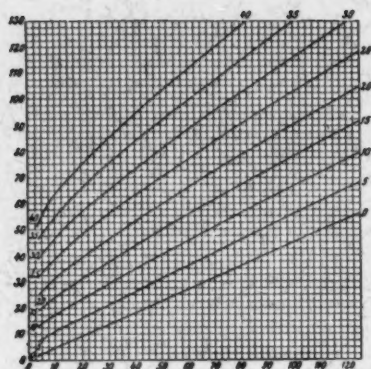


Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN
				Vol. Issue Year
AÉ	Atomnaya énergiya	Soviet Journal of Atomic Energy	Consultants Bureau	1 1 1956
Akust. zh.	Akusticheskii zhurnal	Soviet Physics - Acoustics	American Institute of Physics	1 1 1955
Astr(om), zh(urn).	Antibiotiki	Antibiotics	Consultants Bureau	4 1 1959
Avto(mat), svarka	Astronimicheskii zhurnal	Soviet Astronomy-AJ	American Institute of Physics	34 1 1957
	Automaticheskaya svarka	Automatic Welding	(London)	
	Avtomatika i Telemekhanika	Automation and Remote Control	Instrument Society of America	1 1959
	Biofizika	Biophysics	National Institutes of Health*	27 1 1956
	Biokhimiya	Biochemistry	Consultants Bureau	21 1 1957
Byull. éksp(erim). biol. i med.	Byulleten' éksp(erim)ental'noi biologii i meditsiny	Bulletin of Experimental Biology and Medicine	Consultants Bureau	41 1 1959
DAN (SSSR)	Doklady Akademii Nauk SSSR	The translation of this journal is published in sections, as follows:		
Dokl(ad)y AN SSSR }		Doklady Biochemistry Section	American Institute of Biological Sciences	106 1 1956
		Doklady Biological Sciences Sections (Includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology, microbiology, morphology, parasitology, physiology, zoology sections)	American Institute of Biological Sciences	112 1 1957
		Doklady Botanical Sciences Sections (Includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections)		
		Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology	Consultants Bureau	106 1 1956
		Proceedings of the Academy of Sciences of the USSR, Section: Chemistry	Consultants Bureau	106 1 1956
		Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry	Consultants Bureau	112 1 1957
		Doklady Earth Sciences Sections (Includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections)		
		Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry	American Geological Institute	124 1 1959
		Proceedings of the Academy of Sciences of the USSR, Section: Geology	Consultants Bureau	106- 1 1957-
		Proceedings of the Academy of Sciences of the USSR, Sections: Geology of the USSR, Soviet Mathematics	Consultants Bureau	106- 1 1957-
		Soviet Physics-Doklady (Includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections)	The American Mathematics Society	123 6 1958
		Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections)		131 1 1961
		Wood Processing Industry		
		Telecommunications	American Institute of Physics	106 1 1956
		Entomological Review	Consultants Bureau	106- 1 1956-
		Pharmacology and Toxicology	Timber Development Association	117 1957
		Physics of Metals and Metallurgy	(London)	
		Sechenov Physiological Journal USSR	Massachusetts Institute of Technology*	9 1959
		Plant Physiology	American Institute of Biological Sciences	38 1 1957
		Geochemistry	Consultants Bureau	20 1 1959
		Soviet Physics-Solid State	Acta Metallurgica*	5 1 1957
		Measurement Techniques	National Institutes of Health*	1 1957
		Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences	The Geochemical Society	4 1 1957
			American Institute of Physics	1 1958
			Instrument Society of America	1 1959
			Consultants Bureau	1 1952
Derevoobrabat. prom-st'.	Derevoobrabatnyyavushchaya promyshlennost'			
Éntom(ol), oboz(renie)	Élektrosnyaz			
Farmakol. (i) toksikol(ogiya)	Entomologicheskoe obozrenie			
FMM	Farmakologiya i toksikologiya			
Fiziol. zhurn. SSSR	Fizika metallov i metallovedenie			
(Im, Sechenova)	Fiziol. zhurn. SSSR			
Fiziol(ogiya) rast.	Fiziol. zhurn. SSSR			
FTT	Fiziol. zhurn. SSSR			
Izmerit. tekhn(ika)	Fiziol. zhurn. SSSR			
Izv. AN SSSR,	Izmerit. tekhn(ika)			
O(ol), Kh(im), N(auk)	Izvestiya Akademii Nauk SSSR,			
	Otdelenie khimicheskikh nauk			

Izv. AN SSSR. Otd.) (tekhn.) N(auk): Met(fiz.) i top.	(see Met. i top.) Izvestiya Akademii Nauk SSSR: fizicheskaya	Bulletin of the Academy of Sciences of the USSR, Physical Series	Columbia Technical Translations	1	1954
Izv. AN SSSR Ser. fiz(ich).	Izvestiya Akademii Nauk SSSR: Seriya fizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series	American Geophysical Union	1	1954
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	Izvestiya of the Academy of Sciences of the USSR: Geologic Series	American Geological Institute	1	1958
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	Soviet Rubber Technology	Research Association of British Rubber Manufacturers	18	1959
Kauch. i rez.	Kauchuk i rezina	Kinetics and Catalysis	Consultants Bureau	1	1960
	Kinetika i kataliz	Coke and Chemistry USSR	Coal Tar Research Association (Leeds, England)	1	1958
	Koks i khimiya		Consultants Bureau	2	1952
			American Institute of Physics	1	1957
Kolloidn. zh(urn).	Kolloidnyi zhurnal	Colloid Journal	Acta Metallurgica	6	1958
Metalov. i term. obrabot. metal.	Kristallografiya	Soviet Physics — Crystallography	Acta Metallurgica	1	1957
	Metalovedenie i termicheskaya obrabotka metallov	Metal Science and Heat Treatment of Metals	Eagle Technical Publications	1	1960
Met. i top.	Metallurg	Russian Metallurgy and Fuels	American Institute of Biological Sciences	1	1957
Mikrobiol.	Metallurgiya i topliva	Microbiology	American Institute of Physics	26	1959
OS	Mikrobiologiya	Optics and Spectroscopy	American Institute of Biological Sciences	1	1958
	Optika i spektroskopiya	Soviet Soil Science	British Scientific Instrument Research Association	1	1959
	Pochvovedenie	Instrument Construction		1	1957
	Pribrostroenie	Instruments and Experimental Techniques	Instrument Society of America	1	1957
Pribyori i tekhn. eksperimenta)	Pribyori i tekhnika eksperimenta	Applied Mathematics and Mechanics	American Society of Mechanical Engineers	1	1958
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika				
PTÉ	(see Pribyori i tekhn. éks.)	Problems of the North	National Research Council of Canada	1	1957
Radiolektkh.	Problemy Severa	Radio Engineering	Massachusetts Institute of Technology*	12	1957
Radiolektkh. i élektronika	Radiolektkhika	Radio Engineering and Electronics	Massachusetts Institute of Technology*	2	1959
	Stanki i instrument	Machines and Tooling	Production Engineering Research Assoc.	1	1959
	Stal'	Stal' (In English)	Iron and Steel Institute	1	1959
Stek. i keram.	Steklo i keramika	Glass and Ceramics	Consultants Bureau	13	1956
Svaroch. proizvo	Svarochnoe proizvodstvo	Welding Production	Society for Industrial and Applied Mathematics	4	1959
Ter. vroyat. i prim.	Teoriya veroyatnostei i ee primeneniye	Theory of Probability and Its Applications	British Welding Research Association	1	1956
			Society for Industrial and Applied Mathematics	1	1956
Tsvet. Metall	Tsvetnyye metall	Nonferrous Metals	Primary Sources	1	1960
UFN	Uspekhi fizicheskikh Nauk	Soviet Physics — Uspekhi (partial translation)	American Institute of Physics	66	1958
UKh	Uspekhi khimii	Russian Chemical Reviews	The Chemical Society (London)	1	1960
UMN	Uspekhi matematicheskikh nauk	Russian Mathematical Surveys	London Mathematical Society	15	1960
Usp. fiz. nauk	(see UFN)				
Usp. khim(ii)	(see UFN)				
Usp. matem. nauk	(see UMN)				
Usp. sovr. biol.	Uspekhi sovremennoi biologii	Russian Review of Biology	Oliver and Boyd	48	1959
Vest. mashinostroeniya	Vestnik mashinostroeniya	Russian Engineering Journal	Production Engineering Research Assoc.	4	1959
Vop. gem. i per. krovi	Voprosy gematologii i perelivaniya krovi	Problems of Hematology and Blood Transfusion			
Vop. onk.	Voprosy onkologii	Problems of Oncology	National Institutes of Health*	1	1957
Vop. virusol.	Voprosy virusologii	Problems of Virology	National Institutes of Health*	1	1957
Zavodsk. lab.(oratoriya)	Zavodskaya laboratoriya	Industrial Laboratory	National Institutes of Health*	1	1957
ZhAKh Zh. anal(it), khimii	Zhurnal analiticheskoi khimii	Journal of Analytical Chemistry USSR	Instrument Society of America	25	1959
ZhETF	Zhurnal éksperimental'noi i theoreticheskoi fiziki		Consultants Bureau	7	1952
Zh. éksperim. i teor. fiz.	Zhurnal fizicheskoi khimii	Soviet Physics—JETP	American Institute of Physics	28	1955
ZhFKh Zh. fiz. khimii	Zhurnal fizicheskoi khimii	Russian Journal of Physical Chemistry	The Chemical Society (London)	7	1959
ZhMEi Zh(urn), mikrobiol. i epidemiol. i immunobiol.	Zhurnal mikrobiologii, épidemiologii i immunobiologii	Journal of Microbiology, Epidemiology and Immunobiology	National Institutes of Health*	1	1957
ZhNKh	Zhurnal neorganicheskoi khimii	The Russian Journal of Inorganic Chemistry	The Chemical Society (London)	1	1959
Zh(urn), neorgan(ich). khim(ii)					
ZhOKh	Zhurnal obshchei khimii	Journal of General Chemistry USSR	Consultants Bureau	19	1949
Zh(urn), obshch(ei) khimii					
ZhPKh	Zhurnal prikladnoi khimii	Journal of Applied Chemistry USSR	Consultants Bureau	23	1950
Zh(urn), prikl. khimii					
ZhSKh	Zhurnal strukturnoi khimii	Journal of Structural Chemistry	Consultants Bureau	1	1960
Zh(urn), strukt. khimii					
ZhTF	Zhurnal tekhnicheskoi fiziki	Soviet Physics—Technical Physics	American Institute of Physics	26	1956
Zh(urn), tekhn. fiz.	Zhurnal vysshei nervnoi deyatel'nosti (im. I. P. Pavlova)	Pavlov Journal of Higher Nervous Activity	National Institutes of Health*	1	1958
Zh(urn), vyssh. nervn. deyat. (im. Pavlova)					

*Sponsoring organization. Translation through 1960 issues is a publication of Pergamon Press.



TABLES AND NOMOGRAMS OF HYDROCHEMICAL ANALYSIS

by I. Yu. Sokolov

Translated from Russian

Upon completion of analytical experiments, every research chemist, whether he uses a "test tube" or a "пробирка," must calculate his findings in the international language of figures in two forms (weights and equivalents), and often three (weights, equivalents and percent-equivalents), and then compare experimental data with theoretical values.

Technicians and statisticians working with the results of hydrochemical analyses performed at different times by different laboratories inevitably face the problem of converting their figures to one system.

All such calculations are considerably simplified by the use of the tables and nomograms in this book, originally published by the State Scientific and Technical Press for Literature on Geology and the Conservation of Mineral Resources, Moscow.

All the tables and nomograms are based on analytical results expressed in the form widely used in hydrogeological practice—milligrams per liter (weight form) and milligram-equivalents per liter (equivalent form). For calculation of percent-equivalents, the sum of cation equivalents and the sum of anion equivalents are taken as 100% each. Several new tables are presented for the first time, and the many tables for converting water-analysis results from one form to another make it possible to find the milligram-equivalents for any practically possible content of a component in water, accurate to the second decimal place, and the weight content of substances to tenths of a milligram.

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Introduction

Tables for converting water-analysis results from one form to another

- I. Table for converting hardness, expressed in German degrees, into milligram-equivalents
- II. Table for converting milligram-equivalents of Ca^{2+} , Mg^{2+} and HCO_3^- into German degrees of hardness
- III. Tables for converting milligrams into milligram-equivalents
- IV. Tables for converting milligram-equivalents into milligrams
- V. Tables for converting oxides to ions
- VI. Tables for converting nitrogen into nitrogen-containing ions
- VII. Table for converting milligrams of NH_3 into milligrams of NH_4^+
- VIII. Table for converting oxidizability with milligrams of KMnO_4 into milligrams of O

Factors for converting the results of water analysis from one form into another

Average value of activity coefficient f_{av}

Nomogram for calculating percent-equivalents

Nomogram for calculating pH from given values of free CO_2 and HCO_3^-

Calculation of aggressive carbon dioxide

Relation between different forms of weak acids in natural waters at different pH values and ionic strengths μ

Factors for converting different forms of expressing aqueous solution concentrations into milligrams and milligram-equivalents

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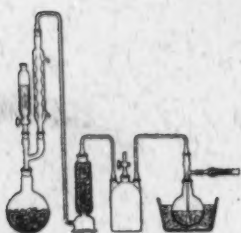
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5-(Butylthiomethyl) Furfuryl Alcohol
5,5'-(Thiodimethylene)bis-2-Furamide
5,5'-Methylenedi-2-Furoic Acid
4,5-Dimethyl-2-Furaldehyde
2,5-Furandimethanol
2,2'-Methylenedifuran
N,N-Diethyl-2-Furamide
5-Carboxy-2-Furanacetic Acid
Methyl 5-Formyl-2-Furoate
4-(5-Methyl-2-Furyl)-3-Buten-2-One
4-(5-Methyl-2-Furyl)-2-Butanone
2-(5-Methylfurfurylamino)Pyridine
5-Nitrofurfuryl Alcohol
5-(Hydroxymethyl)-2-Furoic Acid

3-Aminopyridine
5-(Benzylsulfonylmethyl)-2-Furoic Acid
4-(5-Benzyl-2-Furyl)-3-Buten-2-One
Benzofuran (Coumarone)
N-Methyl-2-Benzofuranmethanamine
2,3-Dimethylindole-5-Carboxylic Acid
Tetrahydro-2,5-Furandimethanol
N,N-Diethyltetrahydrofurfurylamine
Indazole
Indole-3-Carboxaldehyde
3-(3-Piperidinopropyl)Indole
Indole-3-Acetic Acid (Heterouxin)
2,3-Dihydro-2-Methylbenzofuran
5-Methylisatin
2-Methylindole-3-Propionic Acid
2-Isindolineethanol

CONTENTS include

5-Benzyl-2-Furoic Acid
5-(5-Benzyl-2-Furyl)-s-Triazole-3-Thiol
5-Bromo-2-Furoic Acid
2-Furanmethanediol Diacetate
5-(Diethylaminomethyl) Furfuryl Alcohol
Methyl 5-Benzyl-2-Furoate
Methyl 5-(Bromomethyl)-2-Furoate
Methyl 5-(Diethylaminomethyl)-2-Furoate
Methyl 5-Methyl-2-Furoate
Methyl 5-(Propoxymethyl)-2-Furoate
Methyl 2-Furoate
Methyl 5-(Chloromethyl)-2-Furoate
2-Methylfuran (Sylvan)
5-Methyl-2-Furoic Acid
5-(Propoxymethyl)-2-Furoic Acid
Furan

5-(Aminomethyl)-2-Furoic Acid
5-Benzylfurfuryl Acetate
2-Furyl Methyl Ketone
2-Benzylfuran
5-Benzylfurfuryl Alcohol
5,5'-(Thiodimethylene) Di-2-Furoic Acid
2,3-Dimethylfuran
4,5-Dimethyl-2-Furoic Acid
1,3-Difurfurylurea
Diethyl (Tetrahydrofurfuryl) Malonate
Diethyl Furfurylidenemalonate
5-Carboxy-2-Furanpropionic Acid
Methyl Tetrahydro-5-Methyl-2-Furoate
Methyl 4-(Chloromethyl)-5-Methyl-2-Furoate
Methyl 5-(Cyanomethyl)-2-Furoate
5-Methylfurfuryl Alcohol

